Eduard Musin (A9838)

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Adsorption Modeling

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MIKKELIN AMMATTIKORKEAKOULU
Mikkeli University of Applied Sciences

DESCRIPTION

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Abstract

In this study, adsorption was explored to remove toxic metals from wastewaters. The main focus of the research work lies on adsorption process, which is described theoretically and studied experimentally. Theoretical part involves studying of the adsorption concepts, adsorbents and adsorption process modelling. Experimental part of the work was aimed to create a condition which will allow examining the adsorption process by using adsorbents to remove toxic metal from aqueous solution. The experiment was divided on analysing optimum concentration and optimum time periods to remove Zn(II) and Cu(II) from aqueous solution by using studied adsorbents. Secondly, the determination of pH values when adsorbents have the highest adsorption activity was required to study. The gathered data were applied to model adsorption process via kinetic and isotherm adsorption models. The target of research was reached: all results of experimental part were satisfactory to be described and concluded by theory.

Subject headings, (keywords)

Adsorption, adsorbent, adsorbate, isotherm, kinetic, toxicology, metals, zeta potential, ICP

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Tutor	**Employer of the bachelor's thesis**
Aila Puttonen	Laboratory of Green Chemistry, Lappeenranta University of Technology; Mika Sillanpää, Evgenia Iakovleva

CONTENTS

1 INTRODUCTION

It is commonly known that Earth is covered by approximately 70% of water, where only 2,5-3% is unleavened water. The large amount of drinkable water is in hard aggregate condition as ice. Eventually, we have less than 1% of fresh water from those 2,5-3% [1]. This amount of drinkable water should be distributed on the growing population of 7 billion inhabitants on the Earth. In accordance to the size of the planet and the amount of inhabitants, the water is available for all of us. However, if the amount of pollutions caused by the activities of the modern world is taken into account, the situation becomes more complicated. Nowadays water pollution is the main agenda of different countries. Surplus of wastewater and lack of pure water pushes government and citizens to pay more for a sip of fresh water and use it rationally. Water treatment technologies help to decrease and sometimes completely illuminate a harmful effect on the environment, and it helps to make equilibrium in natural water cycle. [1].

Water can be polluted naturally or anthropogenically. Therefore, a selection of wastewater treatment methods is an essential question which is related to the types of wastewater. Generally, wastewater can be divided on domination of organic compound or inorganic matter in it. This research studies inorganic compounds removal from wastewater. In the role of contaminants are toxic metals which are dangerous for the environment and deadly poisonous for humans and animals. Most of the point sources of toxic metals are fuel industry, machinery, traffic, ferrous metallurgy, non-ferrous metallurgy, mining industry, chemical industry, electroplating etc. Contaminants in wastewaters might be different and complex substances. [1]. Therefore, a determination of a method of wastewater treatment for a certain particular case is observed individually. The capacity of all methods of wastewater treatments is essential to analyse theoretically and technically through experiments, which give plenty of data, which help to realize a contaminant reduction dynamics from wastewaters. However, most of those methods are suffering from drawbacks, such as high consumption of reagent and energy, high capital, high operational costs and the resulting sludge which is difficult to dispose of [2]. Consequently, it is necessary to use a method which might be promptly implemented but also cost-effective. In this study adsorption was chosen as a good way for industrial wastewater treatment and removal of toxic metal, because adsorption has

many benefits compared to other methods, such as lower operating cost and simplicity in utilization. The main target of this research work was to study adsorption process theoretically and practically. [2, 3].

Study of adsorption was performed in Laboratory of Green Chemistry, which is a department of Lappeenranta University of Technology. The laboratory is located in Mikkeli. The Head of the Laboratory is Professor Mika Sillanpää. Laboratory of Green Chemistry focuses on studying technologies, such as adsorption, analytics, online monitoring, advanced oxidation processes, electrokinetics and electrochemical technologies. [2].

2 WASTEWATER TREATMENT TECHNOLOGY

The wastewater treatment technologies are aimed to decrease the harmful effect for the environment by organic and inorganic contaminants in water. Treated wastewater should be able to be discharged into the environment or to be used by industries without negative consequences. The wastewater treatment technologies have strong future perspectives which create challenging condition in water treatment development. Therefore, wastewater treatment technologies are on high priority among other technologies. Wastewater treatment technologies can be divided on active and passive methods. The main difference between passive and active water treatment systems is that passive ones use naturally available energy sources, such as photosynthesis, microbial metabolic energy and/or topographical gradient, compared to active ones, which require external sources of energy as electricity. [4].

Active and passive methods

The list of well-known *active methods* includes neutralization, filtration, ion exchange, electrodialyses, solvent extraction, freeze separation and adsorption (Table 1). The word "active" implies that active methods require a lot of maintenance and external energy to carry a treatment process. *Passive wastewater treatment methods* are less efficient than active wastewater treatment methods and usually used as addition to active methods. Passive methods include constructed wetlands, limestone drains and reactive barriers (Table 1). Passive wastewater treatment requires less of technical maintenance

than active ones, which extends the durability of the certain method, but usually service is infrequent. [4].

TABLE 1. Active and passive wastewater treatment methods

Active wastewater treatment	
Neutralization	Treatment with alkalis, acids, lime, soda, ammonia, or etc. to provide desired pH value
Filtration	For suspended and dissolved solids; Filtration occurs by filters from 10^{2} to 10^{-4} μm of particle size
Ion exchange	A reversible chemical reaction in where occurs exchange of ions between a solid substance and the electrolyte solution
Electrodialysis	Based on a concentration changing of the electrolyte solution by influence of current; used for the desalination of water, i.e. from toxic metal salts
Solvent extraction	Based on relative solubility of a contaminant in two immiscible liquids
Freeze separation	Separation of two liquefy substances based on varied melting points
Adsorption	Adhering of contaminant(s) on surface of material with adsorption properties
Passive wastewater treatment	
Constructed wetland	Artificial wetland with plants which can retain contaminants on their roots
Limestone drains	Closed channels filled with limestone to increase alkalinity of wastewater
Reactive barrier	Underground barrier/wall with organic or inorganic reactants which is constructed on highly contaminated groundwater flow

In this study, adsorption is chosen as a method of toxic metals removal from aqueous phase because it has significant benefits among other wastewater treatment methods. On the one hand, operating costs are low and utilization is simple; on the other hand, adsorption is a highly efficient method in removing very low levels of toxic metals from dilute solutions. High selectivity, minimum production of by-products such as chemical sludge, and regeneration ability are the most valuable point for adsorption. [3, 5].

3 POLLUTION AND SOURCES

Transportation of heavy metals into the environment occurs as a result of natural processes of distribution. Nevertheless, the anthropogenic emissions of heavy metals take even stronger position compare to natural sources. [1, 6].

Sources of toxic metals

The significant amount of heavy metals comes from [1]:

- Fuel industry and fuel machinery, such as V, Hg, Pb
- Traffic → Pb, Hg, V
- Ferrous metallurgy and non-ferrous metallurgy → Fe, Cr, Cu, Mo
- Mining industry → Cu, Zn, Fe
- Chemical industry → Zn, Cd
- Electroplating → Zn, Cu
- Rubber, plastic and wood industries → Se, Pb

From the whole list of heavy metals from industrial units, the large amounts of Pb, Zn and Ni come into the environment in comparison with others (respectively over 33, 13 and 6 thousand tons/year in the countries of West Europe). Currently, anthropogenic flows of Pb, Hg, Cd, Ni, V, As, Sb and Se prevail over natural sources. However, the anthropogenic flow of toxic metals into the environment is based on order [4]:
Cd>Pb>As>Zn>Ni>Co>Se

All toxic metals are dangerous, especially when occupational exposure limits are exceeded, for example V, Co, Ni, Cu, Zn, Cd, Pb, Zn, As, Se are the most dangerous with oxidation number two (II). Hg and Cr with all oxidation numbers are dangerous. [6]

Nevertheless, for all industries, whose activity and/or by-products consist of toxic metals, exist directives and regulations aimed to control the emission level. The purification of wastewaters is implemented at the source of pollution. EU has directives related to wastewater treatment and discharge, such as "Council Directive 91/271/EEC concerning urban waste-water treatment" which aimed to manage urban and industrial units' wastewaters discharge into the environment. [7].

4 TOXICOLOGY

Collocation "heavy metals" was included into scientific lexicon at the end of 1960th. Also it is named as "toxic metals". From one point of view, the toxic metals are deadly poison for living organisms but, on the other hand, many of them are essential for various living organisms. [6].

4.1 Essential and dangerous elements

Different techniques of chemical analyses and study of biochemical processes allowed determining a biological importance of many elements. All in all, 80 chemical elements including heavy metals such as Mn, Ni, Cu, Cr, V and Zn were identified in the living cells. All of them together with Fe, Co and Mo are a part of the enzymes or enzyme activators. [6]. The individual demand of heavy metals is low, for example in the body of adult a general concentrations of Zn is 12-16 mg, Cu 0.9-2.2 mg, Ni 100-300 μg, Fe 10-18 mg. The excess amounts of heavy metals from natural concentration levels can be a reason of serious disturbances of metabolism. Chemical eco-toxicology pays more attention to those toxic metals, which are amenable to replacing essential elements, bioaccumulating (cumulative effect in the organism) and/or ecological magnification (it is a process of increasing of a chemical element(s) concentration in a living body during a transition from the lower trophic levels (food chain position of an organism) of a certain ecosystem to a higher one. [4, 6]

4.2 Toxic metals

The main importance in toxic metals analyses is to study the element's solubility, essentiality, physiological effect, toxicokinetics, toxicity and nature of a certain metal. For this research work, Zn and Cu were observed. These metals are the most common in

wastewaters of many industries [6]. Allowable EU standard concentrations of Zn and Cu in wastewater from non-domestic sources [8]:

- Zn ≥ 5 g/l
- Cu ≥ 1 g/l

Excessive amounts of toxic metals found in wastewater in high than allowable EU standard concentrations can put a stop to an activity of a certain industry [8].

4.2.1 Zinc (Zn)

Zinc is a chemical element which has a molar mass 65.38; atomic number is 30 in the periodic table with the chemical symbol Zn. All salts of zinc are well dissociated in water. [6].

Essentiality and physiological effect

Zinc is nutritionally essential trace metal and might be labelled as ubiquitous in the environment. Zinc is presented in soil, water, air and most foodstuffs. Deficiency of zinc may cause serious health problems. More than 200 metalloenzymes (enzymes that require metals to carry out normal functioning of metalloproteins) require zinc as a co-factor, non-protein chemical compound aimed for the protein's biological activity. Zinc takes part in many chemical-biologic processes. [6].

Toxicokinetics

Daily recommended dose for adults of zinc in average is approximately 12-16 mg. The natural sources of zinc are usually from food, such as vegetables, fruits and meat. According to essentiality of this element the recommended dose should be covered for the normal vital activity. [6].

Toxicity

All zinc salts are highly toxic to humans and animals. Chlorides ($ZnCl_2$), sulphates (ZnSO4), and zinc oxide (ZnO) can cause severe poisoning of a body. The reason of

high toxicity is toxic ions of Zn^{2+}. 1g of zinc sulphate $ZnSO_4$ is enough to cause a severe poisoning. $ZnSO_4$ poisoning leads to anaemia, growth retardation and infertility. [6].

4.2.2 Copper (Cu)

Copper is a chemical element which has a molar mass 63.55; atomic number is 29 in the periodic table with the chemical symbol Cu. All salts of copper are well dissociated in water. [6].

Essentiality and physiological effect

Copper is widely spread in nature and is a nutritionally essential element. Copper is a component of all living cells and associated with many oxidative processes. It is an essential component of metalloenzymes which take part in haematopoiesis. [6].

Toxicokinetics

For adults the daily intake of copper is varies between 0.9-2.2 mg. The natural sources of copper are vegetables, fruits and meat. Copper is involved in the formation and re-generation of bone tissue. It increases the activity of pituitary hormones, increases the body's defence (for the strengthening of the immune system), and increases the antitoxic function of the liver. Copper has bactericidal properties. [6].

Toxicity

A systematic intake of copper salts, most frequently copper sulphate, may cause hepatic necrosis and death. According to toxicity of copper, it can be pointed that risks to human health from a lack of copper in a body is many times higher than a risk of its excess. [6].

5 BASICS CONCEPTS AND THEORY OF ADSORPTION

The main target for this research work was to study adsorption process theoretically and practically. The concept of adsorption, dynamics of adsorption development, types of adsorption, study of adsorbents, treatment capacity of adsorption and adsorption process

modelling are described in the theoretical part. The practical part contains study of adsorbents, determination of adsorbent concentrations for contaminant removal, preparation of adsorbate solution, initializing a treatment process, sampling, solution analysis, data analysis and adsorption modelling. The most significant part is the modelling of adsorption process. Modelling is based on isotherms of adsorption, adsorption kinetic models and zeta potential. [2, 3].

Adsorption is a surface phenomenon where adsorbent is a substance which adheres another substance on its surface. A substance which accumulates on the surface of adsorbent is named adsorbate. Adsorption might be chemical or physical process, or combination of those, which occurs at the common boundary of two phases, such as liquid-solid, gas-solid, gas-liquid or liquid-liquid. [9]. By other words, adsorption is a change in concentration of a certain substance (i.e. contaminant) at an interface where an initial concentration is decreased. Historically, adsorption has been first observed by C.W.Scheele in 1773 for gases. Lowitz has continued observation of experiments in 1785 for solutions. Currently, adsorption is actively studied by many institutes around the world, for example Laboratory of Green Chemistry, which is a department of Lappeenranta University of Technology ruled by Professor Mika Sillanpää. [2, 10].

Adsorption has importance for industries which work with gas, petroleum, air and water purification. Adsorption is applied for purifications of organics and SO_2 from gas phase. Also water can be extracted from O_2, CH_4, N_2, additionally NO_x can be excreted from N_2. Adsorption is also used for gas separations, such as N_2 from O_2, acetone and C_2H_2 from vent stream, and CO, CH_4, CO_2, N_2, Ar from hydrogen. In the liquid phase, adsorption is applied, for example, for organic and inorganic removal, and decolourization. [11]

5.1 Adsorption mechanism

The classical mechanism of adsorption is divided into three steps (Fig.1): a) diffusion of adsorbate to adsorbent surface, b) migration into pores of adsorbent c) monolayer build-up of adsorbate on the adsorbent. Fig.1 presents the process of adsorbate distribution. Step 1 occurs diffusion of adsorbate on the adsorbent surface by intermolecular forces between adsorbate and adsorbent. The second step involves migration of adsorb-

ate into pores of adsorbent. During the last step, when the adsorbate's particles are distributed on the surface and filled up the volume of pores, particles of adsorbate are building up the monolayer of reacted molecules, ions and atoms to the active sites of adsorbent. [2, 3].

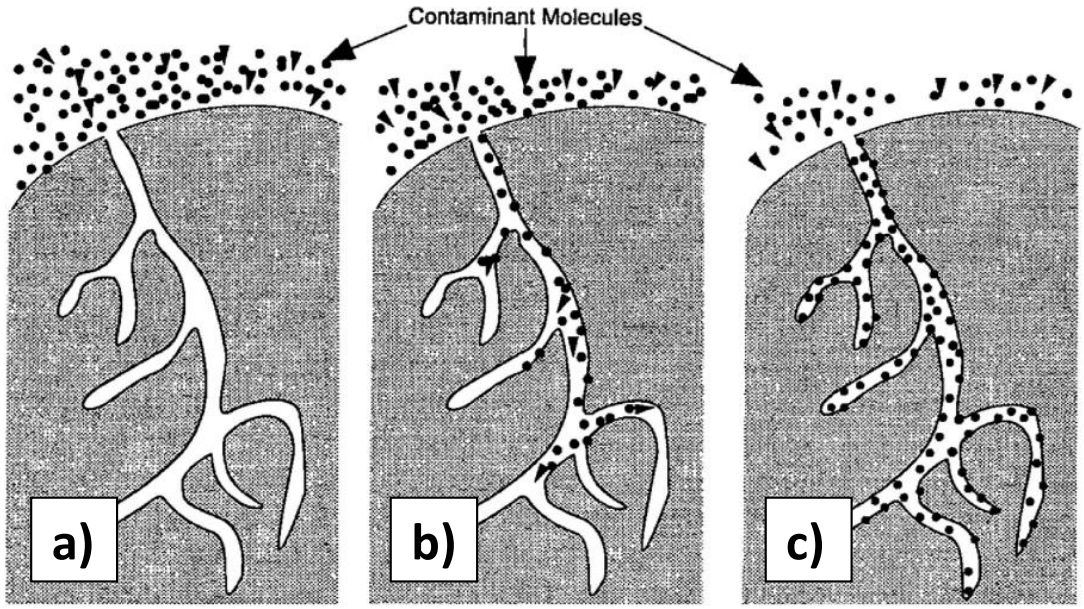

FIGURE 1. Three steps of adsorption mechanism: a) diffusion of adsorbate to adsorbent surface b) migration into pores of adsorbent c) monolayer build-up of adsorbate on adsorbent [11]

5.2 Physisorption and chemisorption

The nature of adsorption depends upon the forces which act between adsorbent and adsorbates. The adsorption forces are a key factor in defining whether the adsorption is physical or chemical. Occasionally, it is complicated to identify what type of adsorption is predominating in a certain situation. Sometimes it might be a combination of chemisorption and physisorption. [5, 9]

Physisorption

Physical adsorption is reversible and rapid. Molecules are holding to the surface by van der Waals forces of attraction (intermolecular forces and interatomic interactions with the energy of 10-20 kJ/mol). Therefore, the lack of interaction energy may break the

bond between adsorbent and adsorbate, for example by mechanical movement of the interface. Consequently, the most valuable parameters for physisorption are the pore size, pore structure, pore volume, and surface area. Physisorption prevails at low temperatures, and activation energy is 5-10 Kcal/mol. [5, 9]

A mechanism of hydrogen storage on the surface of highly porous material is shown in Figure 2. The molecules of hydrogen accumulate at the surface of the porous material without reacting chemically with it. [12]

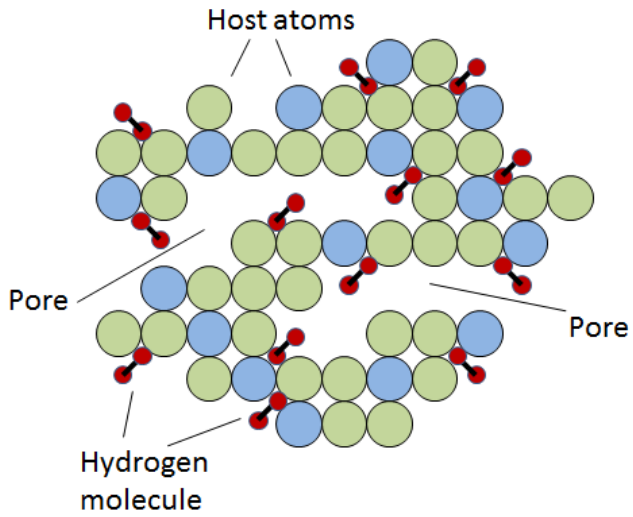

FIGURE 2. Mechanism of hydrogen storage by physisorption [12]

Chemisorption

A specific surface area of phases, types of active sites, number of active sites, and stability of active sites are predominantly valuable for chemisorption. Chemical adsorption occurs as a result of chemical reaction between molecules and atoms of the adsorbate and adsorbent. Chemisorption is irreversible because chemically adsorbed molecules are not able to move on the surface of within interface. The main advantages are high selectivity of separation and the ability to treat exceptionally small concentrations of solute. Chemisorption accelerates by elevated temperature where activation energy varies between 10-100 Kcal/mol. [5, 9]

A mechanism of hydrogen storage by using chemisorption onto certain metals was taken as example. In figure 3 (a) hydrogen molecules attached on the surface of the

material. Then molecules split into separate atoms (Fig.3 (b)). The hydrogen atoms distribute randomly in the structure of material (Fig.3 (b)). Finally, hydrogen compounds adopt an ordinary arrangement and form ionic, covalent or metallic bonds with the metal atoms (Fig 3 (c)). [12]

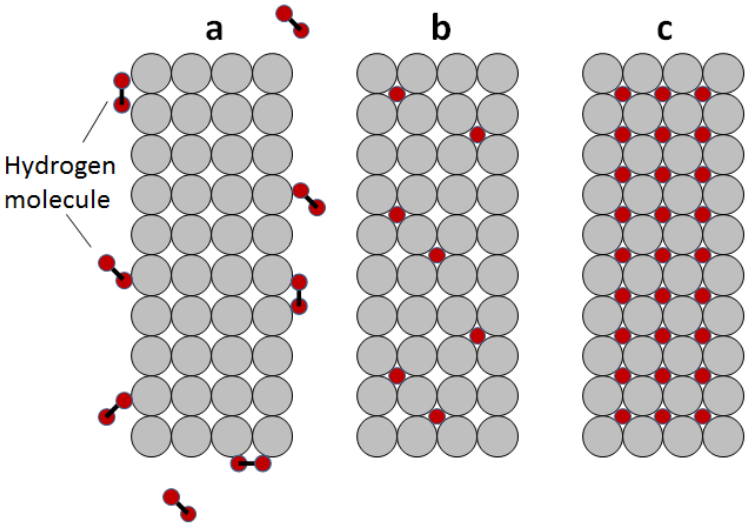

FIGURE 3. Mechanisms of hydrogen storage by chemisorption. Modified from [12]

6 ADSORPTION PROCESS MODELLING

Adsorption process modelling helps to identify the removal efficiency of adsorbent. Adsorption modelling is applied to describe the experimental data by using adsorption isotherm and kinetic models. Additionally zeta potential is applied for analysing adsorption process. [11]

6.1 Adsorption Kinetics

The kinetic equations of the chemical reaction show the dependence of the reaction rate on the concentrations of the reactants. The kinetic equation of chemical reaction is determined experimentally by using gathered data from the experiment. The study of adsorption kinetics is important because it provides valuable information and describes the mechanism of the reaction. [2]

Adsorption kinetics helps to determine the overall rate of the adsorption process. The mechanism of adsorption process is investigated by kinetic equations, for example zero-, first- and second-order, pseudo-first- and pseudo-second-order. [4, 13] In this study

pseudo-first- and pseudo-second-order reactions were observed, as the most common cause for adsorption modelling. [13]

Pseudo-first-order Kinetic Model

This model is based on equation:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (1)$$

Where k_1 (l/min) is the rate constant of pseudo-first-order, q_e, (mmol/g) represents equilibrium adsorption capacity, q_t (mmol/g) adsorption capacity at time *t*, and e is exponential function. [11]

Pseudo-second-order Kinetic Model

It can be represented as the following equation:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (2)$$

Where k_2 (l/min) is the rate constant of pseudo-second-order, q_e, (mmol/g) represents equilibrium adsorption capacity, and q_t (mmol/g) adsorption capacity at time *t*. [11]

6.2 Adsorption Isotherms

Adsorption isotherms show the dependence of the amount of adsorbed substance from the solution concentration at constant temperature. The adsorption capacity of adsorbent is determined by using the adsorption isotherm models. The most commonly used isotherms for modelling adsorption processes in liquid phase are the Freundlich and Langmuir isotherm models. [11, 13]

Adsorption isotherms help to design experimental system and to evaluate it, based on isotherm models, such as Freundlich and Langmuir isotherm models, and to find out a deviation between experimental data and isotherm models. Adsorption isotherms are helping to describe surface processes of adsorbent, type of adsorbate monolayer or multilayer and capacity of adsorbent, which were used for this work. [11, 13]

Langmuir Isotherm Model

According to the Langmuir model, adsorption occurs uniformly on the active sides of the adsorbent. The Langmuir isotherm model is described by the following formula:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

Where, q_e (mmol/g) is equilibrium adsorption capacity (mg/l), C_e is equilibrium concentration (mg/l), q_m is maximum adsorption capacity (mg/g), and K_L (l/mg) is the Langmuir's constant. [2, 5, 11]

Freundlich Isotherm Model

The Freundlich isotherm is an empirical model that is based on adsorption on a heterogeneous surface (surface with varying properties i.e. any surface properties are distributed unevenly, for example surface energy is different at certain points). This is applicable to a non-ideal sorption as well as a multilayer sorption process. The Freundich model is given by the following equation [11, 13]:

$$q_e = K_F C_e^{1/n_F} \quad (4)$$

Where K_F is Freundlich affinity constant (based on (mmol/g)/(l/mmol)^{n_F}), n_F is the Freundlich heterogeneity factor, q_e (mmol/g) is equilibrium adsorption capacity (mg/l), C_e is equilibrium concentration (mg/l), and $1/n_F$ is the heterogeneous factor. [11, 13]

6.3 Zeta Potential

Zeta potential is a measure of the magnitude of the electrostatic interrelation (repulsion or attraction) between particles. Analysing zeta potential helps to get a clear picture of mechanisms in cases of flocculation, aggregation or dispersion. [11]

Zeta potential helps to determine adsorption properties when adsorbent's particles are mixed in liquids. Particles in liquids or suspensions are usually charged. A surface of an adsorbent particle is negatively or positively charged, and it is surrounded by ions with the opposite charge. Therefore, a charge of a particle is essential in adsorbent analyses to evaluate adsorbent potential. Zeta potential analysis helps to identify an isoelectric point of adsorbent. Isoelectric point is a pH value at which adsorbent does not have a charge to attract adsorbate. [11]

Figure 4 shows dependency of zeta potential (mV) at different pH values. At pH 6 the curve does not have any charge (mV); this is named as isoelectric point. If zeta potential is negatively or positively high it means that attraction charge is stable and can retain ions stronger.

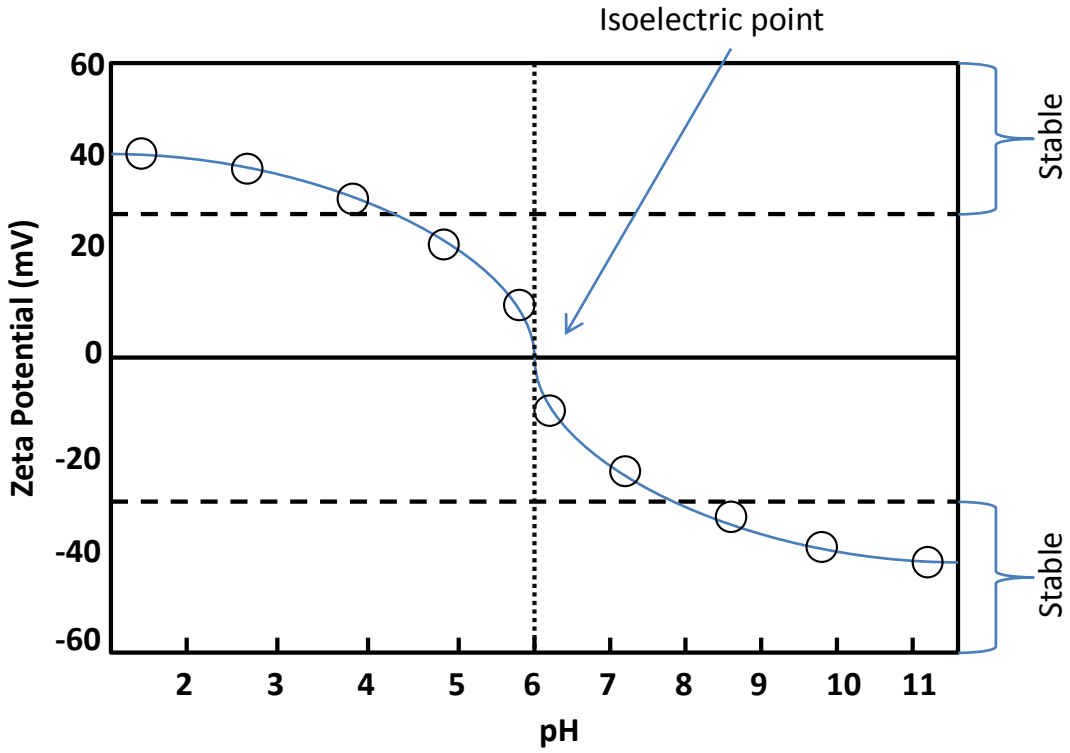

FIGURE 4. Zeta potential, isoelectric point

6.4 Adsorbents

Adsorbent - a substance with the adsorption properties. The important properties of adsorbent are selectivity, high capacity, chemical and thermal stability, low solubility in the carrier solvent, regeneration ability, physical stability and low cost. [3, 9]

Activated carbon

Activated carbon (Fig. 5) is the well-known adsorbent which is widely used in many industries, such as water treatment and medical production. It has exceptionally strong adsorption properties and complicated structure. Activated carbon can be produced by physical or chemical activation from material such as coal, lignite, nutshells, peat, wood and petroleum pitches. [2, 14, 15]

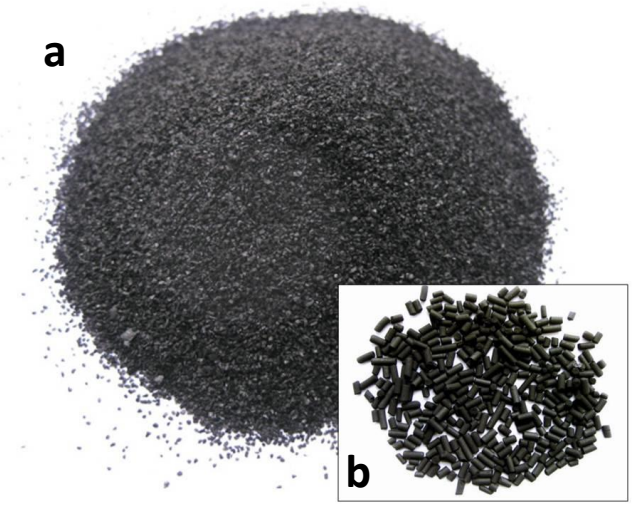

FIGURE 5, Activated carbon, a) milled carbon which is powder, b) granulated active carbon [16]

Zeolite

Zeolites (Fig.6) are complex aluminosilicate containing oxides of alkali and alkaline earth metals. Natural and synthetic zeolites have a frame structure which give unique adsorption properties. Zeolite is widely used adsorbent for different purposes. It is applied for unsurpassed gas driers and cleaners, organic and inorganic compound removal from liquids and gases. Zeolite might be natural, modified natural or synthetic. Physicochemical properties of zeolite are thermal stability, high adsorption potential at low temperatures, and extremely powerful sorption capacity to extract water from gases. [2, 17]

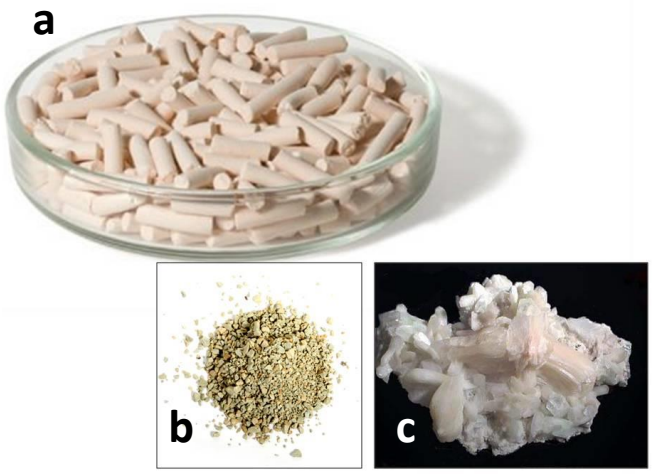

FIGURE 6. Zeolite, a) synthetically manufactured in granules, b) crushed natural zeolite and c) mineralized zeolite [17]

Activated alumina

Activated alumina is a refractory compound of Al_2O_3 (Fig. 7). Activated alumina is active amorphous oxide with different adsorption properties. It is hydrophilic and has strongly developed pore structure. It is produced from aluminium hydroxide by dehydrating. It is used in purification of liquids and gases to remove, for example fluoride, arsenic, selenium. Also in industry it is used as drier for natural gas and other gases in gaseous and liquid phases. Important properties are thermal stability, easy manufacturing and regeneration. [2, 18, 19]

FIGURE 7. Activated alumina, manufactured in spheres form [18]

Silica gel

Silica gel (Fig.8) is a solid adsorbent which forms as spherical translucent-matte beads in sizes from 3 to 8 mm. The structure of silica gel is highly porous formed by tiny spherical particles. The chemical composition is SiO_2. Silica gel is used to adsorb water vapour and organic solvents and non-polar liquids. In gas and liquid chromatography it is used for the separation, for example alcohols, amino acids, vitamins, antibiotics. Large-pore silica gels are used as catalyst supports. [2]

FIGURE 8. Spherical transparent beads of silica gel [20]

Chitosan

Chitosan (Fig. 9) is organic adsorbent, which is made from crab-shell chitin. It has high efficiency of toxic metals removal from wastewater. Chitosan is surprisingly cheap adsorbent with its strong adsorption properties. Chitosan can adsorb 60 different metal ions from wastewater, such as Be(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), Y(III), Ag(I), Cd(II), In(III), Pb(II), Bi(III), Th(IV). [2, 21]

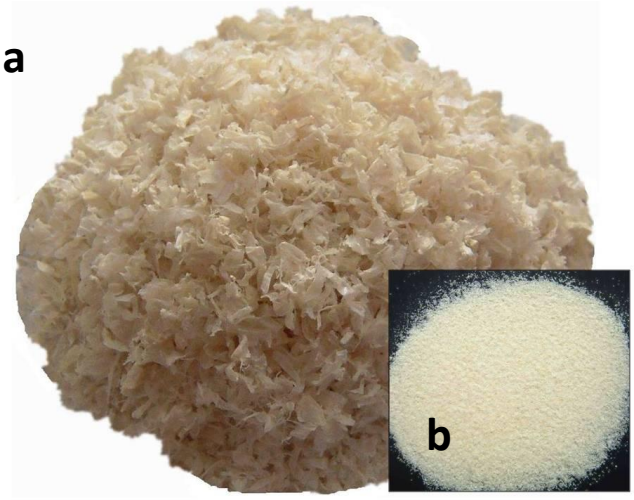

FIGURE 9. Chitosan produced as flakes (a) and as powder (b) [22]

The list of commonly known and widely used adsorbents with strong adsorption properties can include biosorbents which are based on physicochemical process where contaminant settles on cellular structure. Sources of biosorbents are agricultural residues, algae plants, microbial species, yeasts and fungi. [23]. Municipal sewage sludge and

industrial wastes can be considered as low-cost adsorbents with powerful adsorption properties which can be used for wastewater treatment purposes. [2]

Not all adsorbents have naturally strong sorption capacity to remove contaminants. Some of them cannot work as adsorbents without pre-treatment. Pre-treatment is modification which might be chemical, mechanical and/or thermal. [10]

7 ADSORPTION MODELING

The experimental study of adsorption process was organized by Laboratory of Green Chemistry. Study of adsorbents was focused on adsorbent retention time, adsorbent stability, adsorbent concentration, a contact time of adsorbent and adsorbate, dependency on adsorption capacity of pH.

The target of the modelling was to identify the adsorption isotherm and kinetic models which can describe the experimental data gathered from ICP (inductively coupled plasma optical atomic emission spectrometry) analysis. Adsorption process modelling was based on Langmuir's and Freundlich's isotherm models. Pseudo-first-order and pseudo-second-order kinetic models were applied to study kinetics. Zeta potential was used to determine an isoelectric point of adsorbents.

Adsorption process modelling is a complex task which was separated for this work on:

1) Identifying the minimum concentration of adsorbent in the solution with maximum adsorption capacity of toxic metal removal
2) Identifying time periods when the chosen concentration of adsorbent in the solution is the most efficient for toxic metal removal
3) Modelling adsorption process through adsorption isotherm and kinetic models, and zeta potential determination

Experimental work

Preparation of experiment was based on batch method for analysing adsorption process. This method requires placing together adsorbent and adsorbate in the same space with constant mixing. Inductively coupled plasma optical atomic emission spectrometry

(ICP-OES) model iCAP 6000 Series (Fig. 30, 31) was applied to analyse the concentration of metals in solutions. Gathered data from ICP was used for adsorption isotherm and kinetic modelling. Isoelectric point (pH value when a certain molecule or surface carries no electric charge) was measured by Zetasizer Nano Series model ZEN 3600 (Fig. 32, 33).

Mass of adsorbent

The minimum concentration of adsorbent in solution which has a maximum adsorption capacity of toxic metal removal was needed to identify. In the role of adsorbents, based on initial experiments two adsorbents were chosen and labelled as X1 and X2. Those adsorbents are close to zeolites structure (Table 2). The masses of adsorbent were 0.1, 0.25, 0.5, 0.75, 1, 1.5, 2, 2.5 and 3 g corresponding concentrations 2, 5, 10, 15, 20, 30, 40, 50 and 60 g/l. The adsorbent masses were weighted by scales (Fig. 24). Those amounts of adsorbents were placed into 50 ml plastic tubes (Fig. 25).

In the role of adsorbates was a solution of toxic metal salts: Cu((II); $Cu(NO_3)_2*3H_2O$, m=3,781 g) and Zn((II); $ZnSO_4*7H_2O$, m=4,415 g). After weighing the toxic metal salts, the mixture was placed into 1000 ml flask and dissolved by ultraclean water with the addition of 10 ml HNO_3 to stabilize the solution. The final concentration of toxic metal salts in the solution was 1000 ppm (Fig. 26) but the further analysis on ICP required 200 ppm of toxic metals in solution. Therefore, 1000 ppm solution was diluted by ultra clean water and properly mixed in another 1000 ml flask. Then 200 ppm solution was added into 50 ml plastic tubes with adsorbents. The samples were closed and placed onto the rotary shaker with a speed of 100 rpm (Fig. 34) to implement a batch method.

TABLE 2. Adsorbent name and description

Adsorbent name	Description
X1	Zeolite, high concentration of Ca
X2	Zeolite, lower concentration of Ca than X1

The solutions were shaked for 1440 minutes (24 hours). The solutions were sampled with 10 ml syringes, and the samples were injected into 10 ml cylindrical plastic tubes

(Fig. 29) through filters to purify sediment from the solution before ICP analysis (Fig. 28).

For ICP calibration, the calibration solutions at concentrations in 5, 10, 25, 50 and 100 ppm of Cu(II) and Zn(II) were prepared. The calibration solutions were diluted from 1000 ppm of commercial standard solutions bought from Romil LTD. The concentrations dilution for calibration solutions were based on the following formula:

$$C_1V_1 = C_2V_2 \quad (5)$$

ICP analysis was used to determine the toxic metal concentrations in the solution with different amounts of adsorbents after a certain period of time (1440 minutes). When the samples and calibration solutions were placed on ICP's auto sampler (Fig. 10), the last step was to prepare ICP programme on the computer where studied toxic metals' wavelengths were adjusted individually. The results were delivered into Excel sheets.

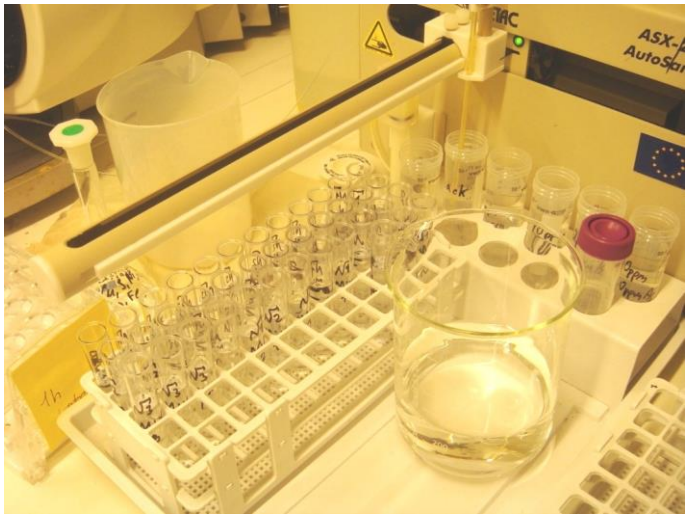

FIGURE 10. AutoSampler ASX-260, synchronized with iCAP 6000 Series

Time for metal removal

The same technique of preparation and measuring was applied with the most efficient mass of adsorbent to identify an ideal adsorption time to remove toxic metals from aqueous solution. The main importance of this step of measurements were identifying time periods when a chosen concentration of adsorbent in the solution is the most efficient for toxic metal removal. Time periods for sampling were 30, 60, 120, 180, 240, 300, 360, 420, 480, 720 and 1440 minutes from the starting moment.

ICP analysis was used to determine the toxic metal concentrations at constant concentration of adsorbent in the solution after certain periods of time. The gathered data from ICP were delivered into Excel file.

Zeta-potential and titration

Isoelectric points and zeta potential of the adsorbents were determined by using Zetasizer Nano. For the experiment, 1,5 g of the adsorbents were weighted, and placed into 50 ml plastic tubes. 50 ml of ultra clean water was added into plastic tubes with adsorbents X1 and X2, and properly mixed by magnet stirrer (Fig. 27) for 5 minutes. Zeta potential determination is done by titration. An initial pH of the solutions was important to be identified before measurements. Solution of X_1 became alkaline and solution of X_2 became acidic in water. Consequently, for a proper titration and identification of the isoelectric points and zeta potential, pH value is important to know in advance. The pH determination was made by pH meter (Fig. 27) and values of initial pH of solutions are shown on Table 3. Thereafter the titrants were prepared based on the scheme:

- ⇨ Alkaline solutions were titrated by HCL (1, 0.1 and 0.001 M)
- ⇨ Acidic solutions were titrated by NaOH (1, 0.1 and 0.001 M)

TABLE 3. Adsorbent pH concentration of 30g/l of adsorbent dissolved in water

Adsorbent name	pH
X_1	8,529
X_2	3,834

Before titration, to define zeta potential in the pH range 1-10:

- X1 had an addition of NaOH until 9,5
- X2 had an addition of HCl until 1,8

Eventually, the gathered data were received in graph format.

Modelling adsorption

All gathered data from ICP analyses (Tables 4, 6 and 8) were used to form adsorption isotherm and kinetic models. Calculations were performed in Excel programme based on adsorption isotherm and kinetic equations.

8 RESULTS AND DISCUSSION

In this research, the main targets were to analyse the minimum concentration of adsorbent in the solution with maximum adsorption capacity for toxic metal removal and identifying time periods when a certain concentration of adsorbent in the solution is the most efficient for toxic metal removal. It helps to evaluate the demand on adsorbent in a certain case for the further rational usage of it and to decrease expenses. Gathered experimental results can be used for large scale adsorption process designing. Another target was to model adsorption process through adsorption isotherm and kinetic models, and zeta potential determination. The results from these experiments can describe the behaviour of adsorbent in definite condition, its stability, surface area and ability to adsorb.

8.1 Optimum concentration of adsorbent

The efficiency of adsorbents X1 and X2 for removal of toxic metals from the solution were analysed by ICP, which gave a clear data about how the concentration of adsorbent is influencing on removing of toxic metals (Fig. 11). The most efficient amount of both adsorbents to remove Cu(II) and Zn(II) was 50 g/l in Figure 11. This concentration can remove 85% of studied toxic metal from solution by adsorbent X1 and 99,5% by adsorbent X2. In comparison between 50 g/l and 60 g/l of both adsorbents, they have similar toxic metal removal dynamics from the solution. Consequently, 50 g/l is an optimum concentration of adsorbent in solution for toxic metals removal.

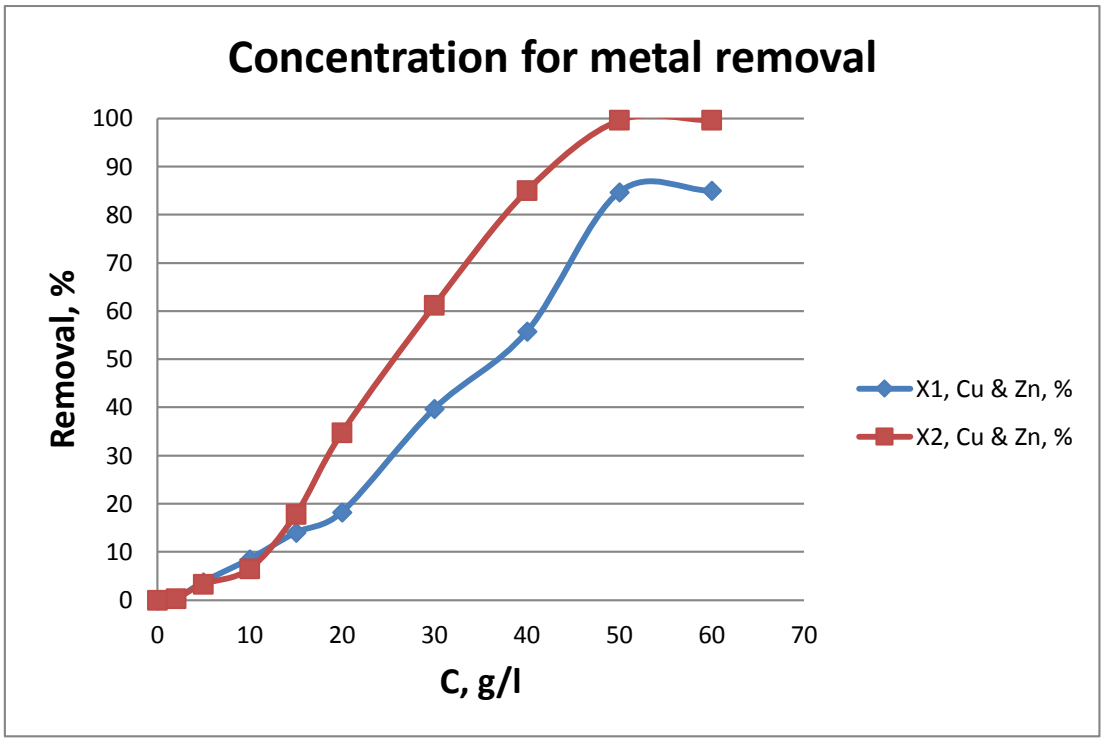

FIGURE 11. Adsorbent capacity at different adsorbent concentrations in solution for toxic metals removal

8.2 Adsorption time

For the second step of measurements by ICP, adsorbent's efficiency was measured on concentration 50 g/l with different time periods: 30, 60, 120, 180, 240, 300, 360, 420, 480, 720 and 1440 minutes. Figures 12 and 13 were built up based on removal capacity of adsorbents at the certain sampling times. In Figure 12 adsorption of Zn(II) by adsorbent X1 goes rapidly at first 120 minutes with good removal capacity which equals 84% at 2,4 pH. After this time, desorption of Zn(II) into the solution takes place in the reaction by the substitution reaction of Zn(II) by Cu(II). Where removal of Zn(II) decreases to 64% at 4,7 pH, then removal capacity for Zn(II) remains constant. Removal of Cu(II) from the aqueous solution starts slower than Zn(II) and moderately rises until 93% at 5,4 pH, then removal capacity becomes constant.

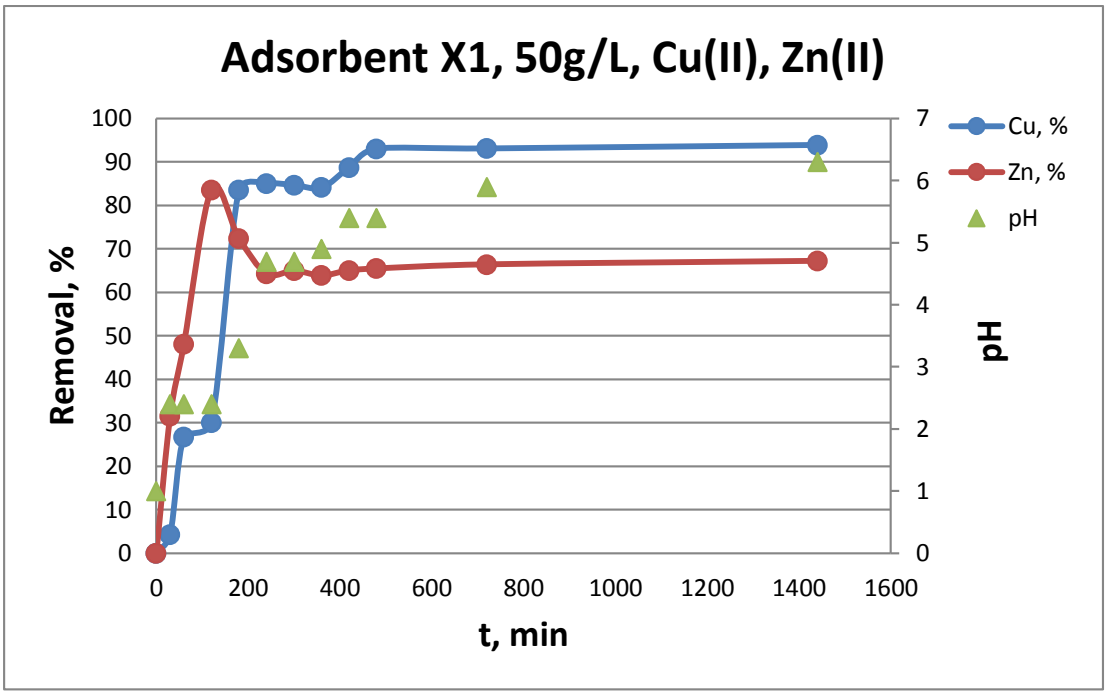

FIGURE 12. Adsorbent X1 50g/l, removal capacity of Cu(II) and Zn(II)

Adsorbent X2 (Fig. 13) is showing quite high removal capacity for Cu(II) and Zn(II) after 120 minutes at pH value 1.4, where removal capacity has raised until 65% for Cu(II) and 88% for Zn(II). From 120 minutes, desorption begins in the solution, which drops adsorption capacity of Cu(II) until 40% and Zn(II) 57%. After 300 minutes adsorption of Zn(II) continues and is predominantly faster than adsorption of Cu(II), increasing to 100% of removal capacity after 1440 minutes at 1.5 pH. From 420 minutes adsorption of Cu(II) continues and slowly increases to 100% after 1440 minutes at 1.5 pH.

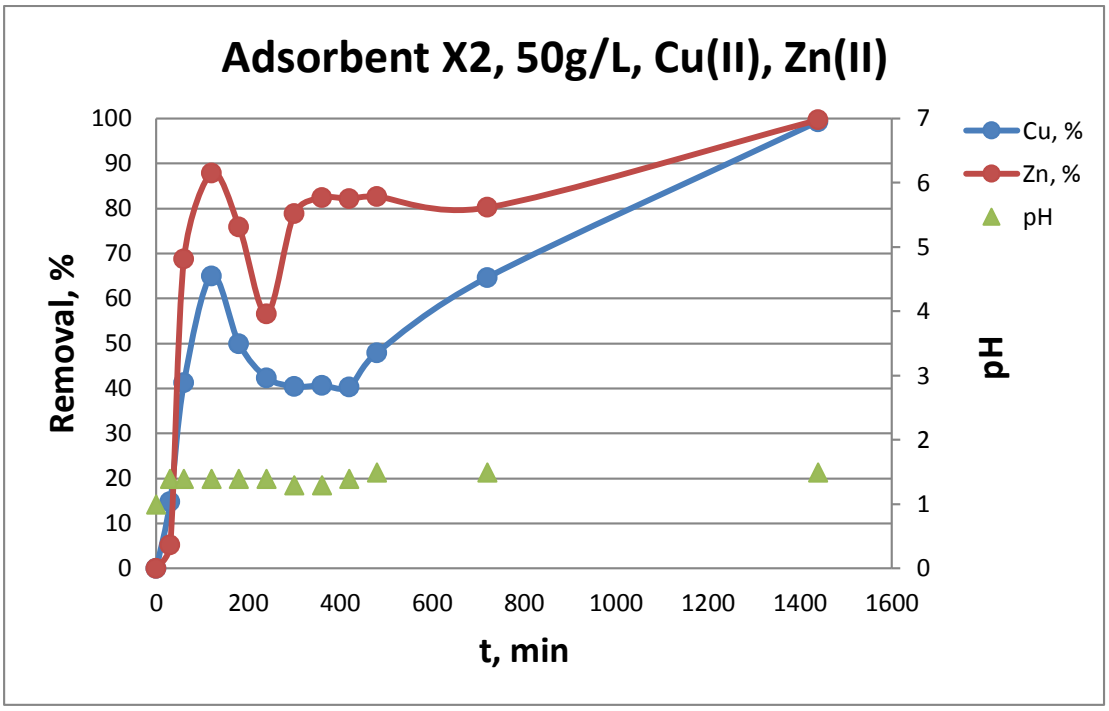

FIGURE 13. Adsorbent X2 50g/l, removal capacity of Cu(II) and Zn(II)

Both adsorbents have shown a good adsorption capacity in removal of Zn(II) and Cu(II) from the solution. Adsorption capacity equilibrium for adsorbent X1 to remove Zn(II) and Cu(II) begins after 420 minutes and for adsorbent X2 after 1440 minutes. In comparison between adsorbents X1 and X2, it can be defined that adsorbent X2 has better adsorption properties in removal of studied toxic metals, compared to X1.

8.3 Adsorption kinetics

Results from ICP analyses were taken for adsorption kinetics modelling based on pseudo-first- (PFO) and pseudo-second-orders (PSO). Pseudo-first-order and pseudo-second-order models are used to analyse adsorbents efficiency and mechanism of the reaction after certain period of time.

Figure 14 shows the kinetic model of adsorbent X1 for Cu(II). The experimental data deviation from pseudo-second-order is not significant compared to pseudo-first-order. Adsorption continues approximately 480 minutes before equilibrium of adsorption capacity (q_e) is reached. In figure 14 it can be seen that the pseudo-first-order model does not fit the kinetic data. Considering that PSO fits well the experimental data, it can be concluded that process follows two-site-occupancy adsorption mechanism.

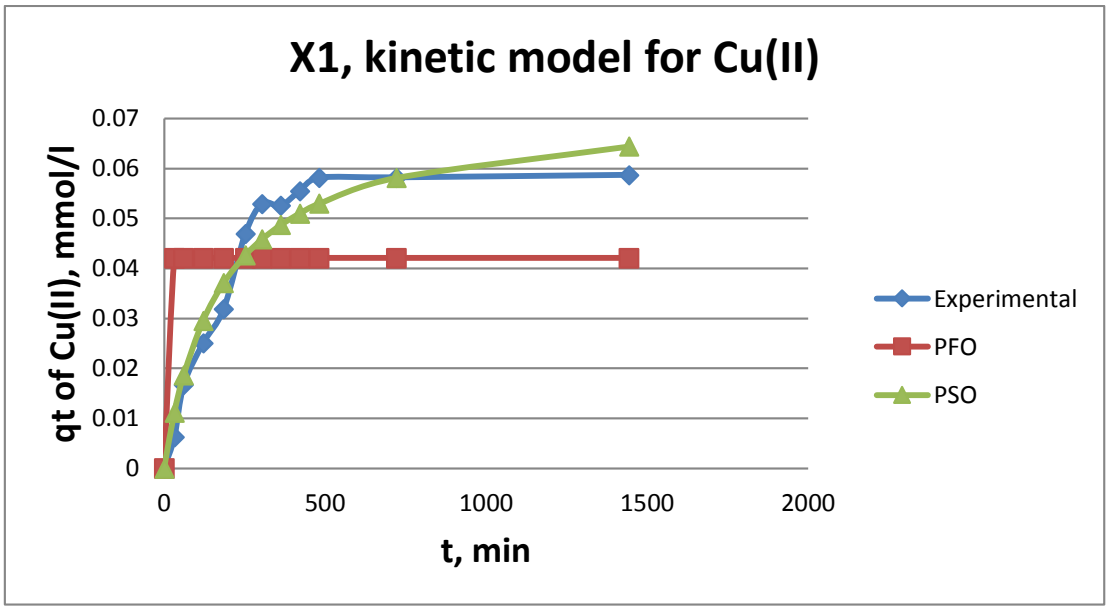

FIGURE 14. Adsorbent X1, kinetic model for Cu

Figure 15 shows the kinetic model of adsorbent X1 for Zn(II). The experimental data approaches PFO well; the deviation between experimental data and PFO model is small especially after 180 minutes. As the PFO model fits well to experimental data, the surface area processes can be defined as mono-site-occupancy adsorption mechanism.

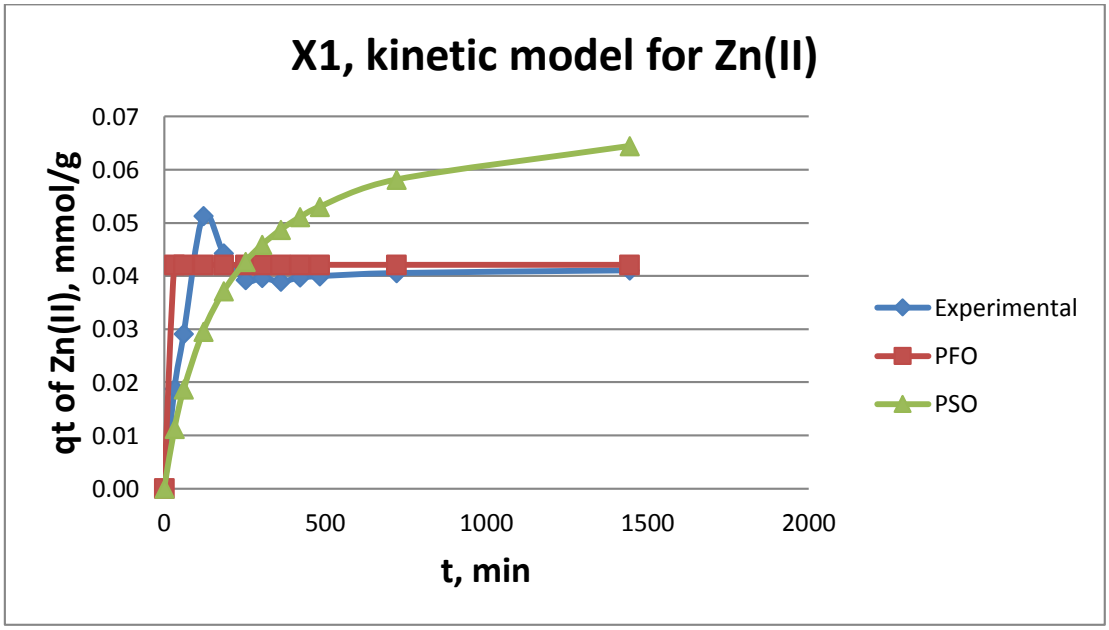

FIGURE 15. Adsorbent X1, kinetic model for Zn

Figure 16 shows the kinetic model of adsorbent X2 for Cu(II). The experimental data deviation from pseudo-first- and pseudo-second-orders model is significant. Adsorption continues until approximately 120 minutes, after this time desorption begins, which

continues until approximately 480 minutes. After 440 minutes the chemical reaction is resuming. Models PFO and PSO do not fit to the experimental data.

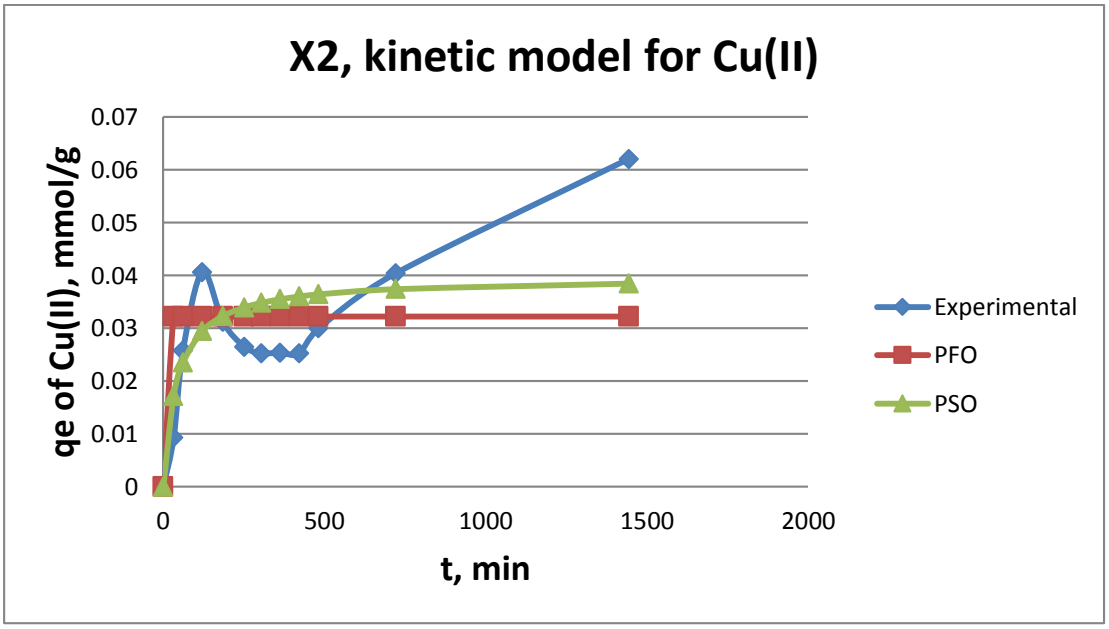

FIGURE 16. Adsorbent X2, kinetic model for Cu

Figure 17 shows the kinetic model of adsorbent X2 for Zn(II). The experimental data deviation from pseudo-first and pseudo-second-orders model is significant but much lower than in Figure 16. Adsorption continues until approximately 120 minutes, after which the desorption begins and continues until approximately 250 minutes. After 250 minutes the adsorption is resuming with a moderate increase. PFO and PSO kinetic models are not able to describe experimental data.

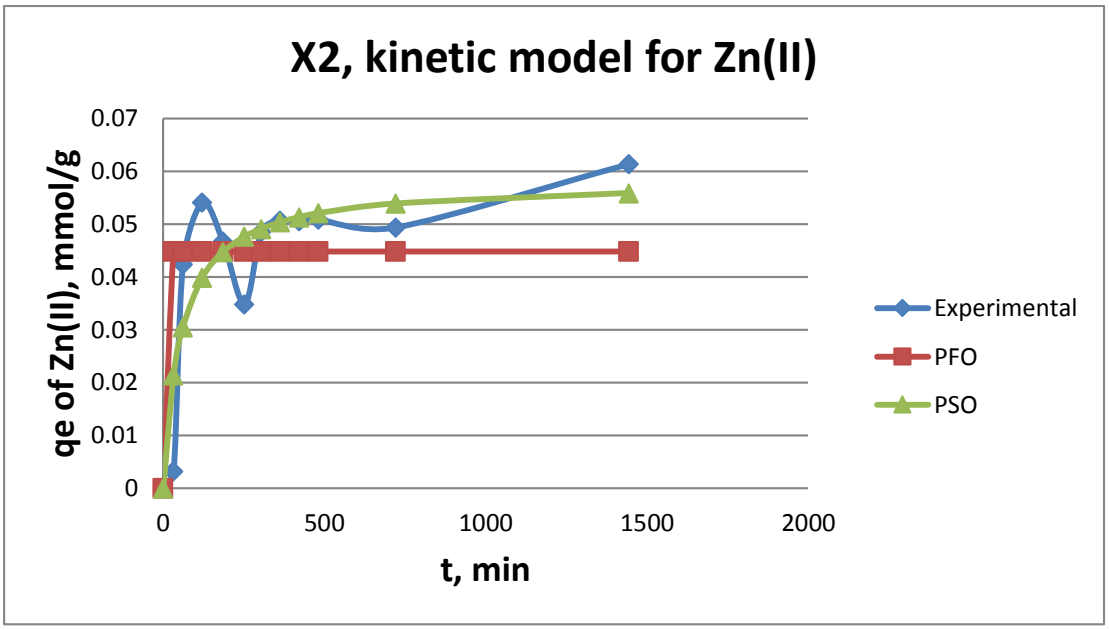

FIGURE 17. Adsorbent X2, kinetic model for Zn

8.4 Isotherm adsorption modelling

Results from ICP analyses were taken for adsorption isotherms modelling based on Langmuir and Freundlich isotherm models. The purpose of Langmuir and Freundlich isotherm models is to analyse adsorbent's specific surface. According to the Langmuir model, adsorption occurs uniformly on the active sides of the adsorbent. The Freundlich isotherm is an empirical model that is based on adsorption on a heterogeneous surface.

Figure 18 is shown isotherm model of adsorbent X1 for Cu(II). The experimental data deviation is lower for Freundlich's isotherm model compared to Langmuir's one. Freunlich isotherm model describes the heterogeneous nature of adsorbent surface. It means that surface of adsorbent has a complex structure. Where, C_e (mmol/l) is equilibrium concentration; q_e (mmol/g) is equilibrium adsorption capacity of Cu(II) (mmol) by adsorbent X1 (g).

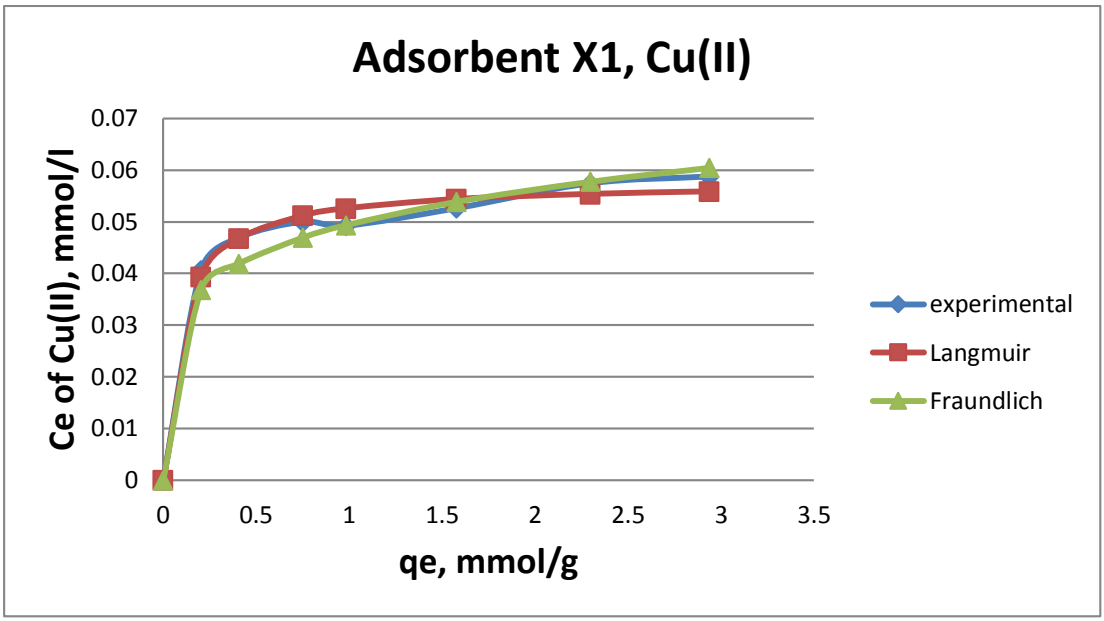

FIGURE 18. Adsorbent X1, isotherm modelling for Cu

Figure 19 is shown isotherm model of adsorbent X1 for Zn(II). The experimental data are closer to Langmuir's isotherm model. Therefore, it can be assumed that the adsorption process occurs uniformly on the active sides of the adsorbent. Where, C_e (mmol/l) is equilibrium concentration; q_e (mmol/g) is equilibrium adsorption capacity of Zn(II) (mmol) by adsorbent X1 (g).

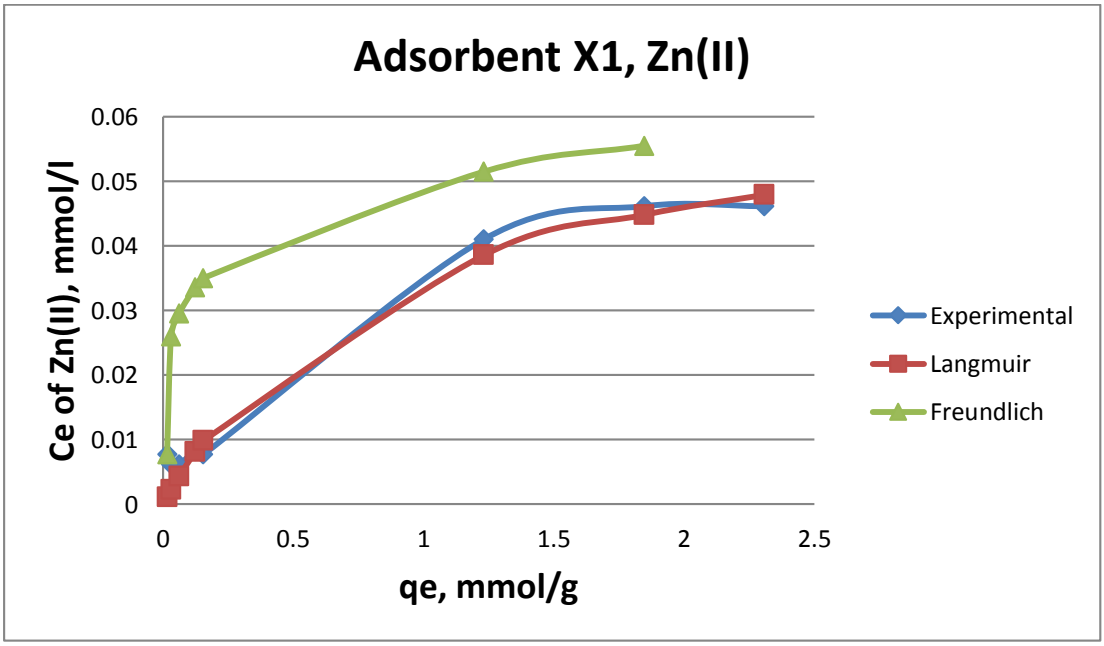

FIGURE 19. Adsorbent X1, isotherm modelling for Zn

Figure 20 is shown isotherm model of adsorbent X2 for Cu(II). The experimental data deviation is lower for Langmuir's isotherm model compare to Freundlich's one. Therefore, it can be assumed that the adsorption process occurs uniformly on the active sides of the adsorbent. Where, C_e (mmol/l) is equilibrium concentration; q_e (mmol/g) is equilibrium adsorption capacity of Cu(II) (mmol) by adsorbent X2 (g).

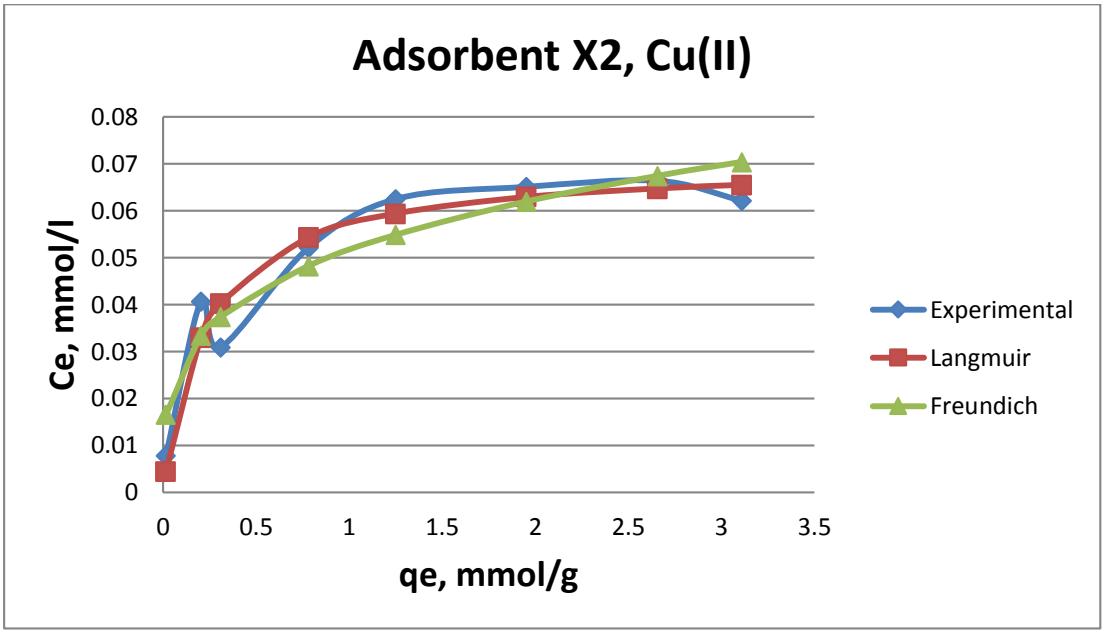

FIGURE 20. Adsorbent X2, isotherm modelling for Cu

Figure 21 is shown isotherm model of adsorbent X2 for Zn(II). In this case, the experimental model is constructed near to Freundlich and Langmuir isotherm models, and to clearly identify attachment to studied model is complicated. Therefore, a clear determination of surface processes between adsorbent and adsorbate is difficult. The suggestion to describe this experimental model is required to apply other isotherm models instead of Freundlich and Langmuir isotherm models. Where, C_e (mmol/l) is equilibrium concentration; q_e (mmol/g) is equilibrium adsorption capacity of Zn(II) (mmol) by adsorbent X2 (g).

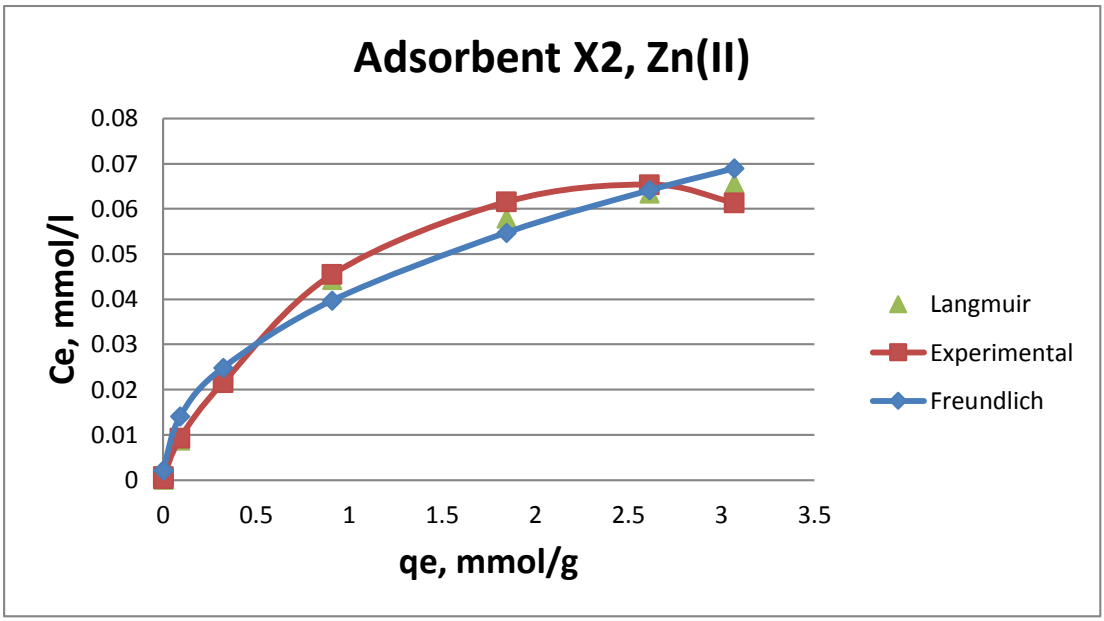

FIGURE 21. Adsorbent X1, isotherm modelling for Zn

8.5 Zeta potential

In figures 22 and 23 is shown data from zeta potential experiments, the stability at different pH values and isoelectric point(s) of adsorbents.

Isoelectric titration graph (Fig. 22) describes adsorbent X1 at concentration 30 g/l in water. Titration was started from 9,6 pH and completed at 1,7 pH. In a role of titrants were HCl 1 and 0.1 M. Isoelectric points of adsorbent X1 in water are 3,3 and 9,3 pH. Consequently, on those pH values adsorbent X1 is inactive. The highest positive zeta potential value is 1,7mV at 1,8 pH and the highest negative zeta potential value is -3,1 mV at 6,4 pH. X1 is the most active and stable at pH value 6,4 where zeta potential equals -3,1. Therefore, negatively charged particles of X1 at this pH value may attract and retain positively charged particles i.e. metals ions.

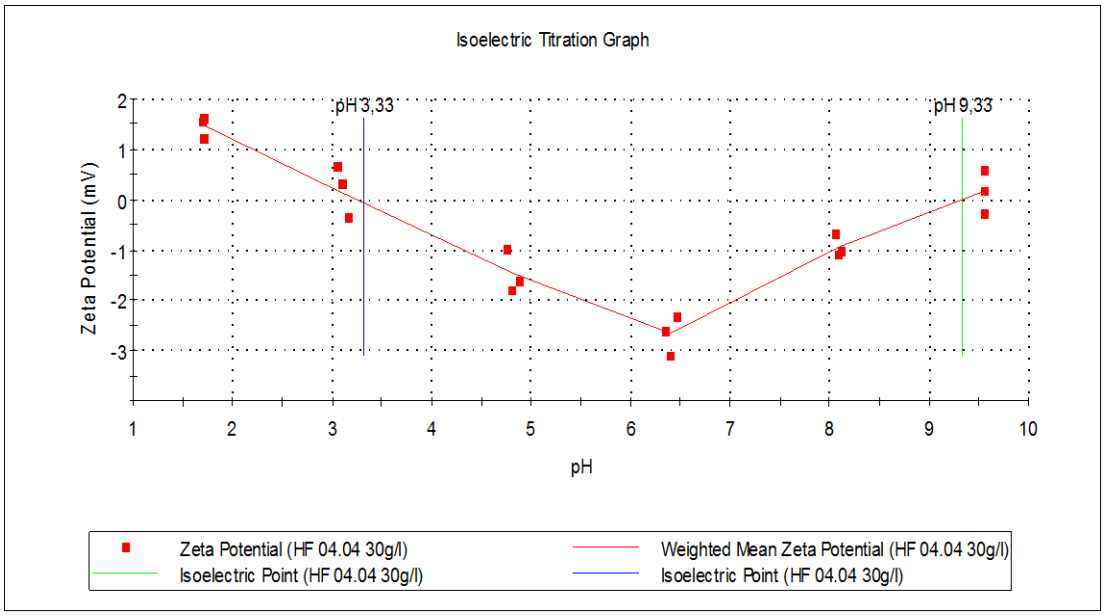

FIGURE 22. Zeta potential measurements of adsorbent X1

Isoelectric titration graph (Fig. 23) describes properties of X2 at concentration 30 g/l in water. Titration was started from 1,8 pH and completed at 9,9 pH. In a role of titrants were NaOH 1, 0.1 and 0.01 M. Isoelectric point of adsorbent X2 in water is 5,2 pH. Consequently, on this pH value adsorbent X2 is inactive. The highest zeta potential value is -6,4 at 1,8 pH. X2 is the most active and stable at pH value 1,8 where zeta potential equals -6,4. In conclusion, negatively charged particles of X2 are behaving similar as X1.

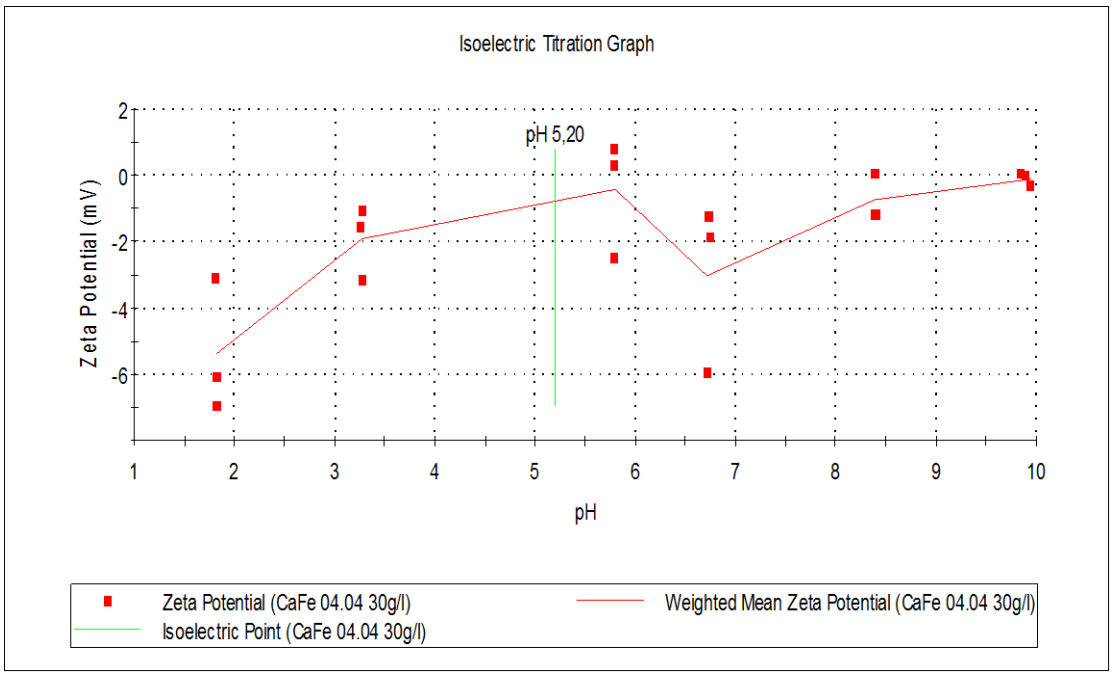

FIGURE 23. Zeta potential measurements of adsorbent X2

9 CONCLUSION

The main target of this research was to study adsorption for toxic metal removal from aqueous solution, where adsorbents X1 and X2 have shown a high removal capacity of Zn(II) and Cu(II) from the solution. The minimum concentration with maximum adsorption properties was 50 g/l for both adsorbents. The most efficient adsorption capacity of adsorbent X1 was at neutral pH value and for X2 acidic pH value. In comparison between the studied adsorbents, X2 has shown brilliant removal capacity, which equals almost 100% in removing Zn(II) and Cu(II) from aqueous solution. Therefore, adsorbent X2 can be applied for further wastewater treatment experiments based on real wastewater contaminated by Zn(II) and/or Cu(II). The results from experiments can be used for large scale adsorption process designing by using preferably adsorbent X2.

BIBLIOGRAPHY

1. Isidorov V. 1997. Introduction to Chemical Eco-toxicology. Saint-Petersburg State University, 54-58.

2. Iakovleva E. Sillanpää M. 2013. The Use of Low Cost Adsorbents for Wastewater Purification in Mining Industries. Environmental Science and Pollution Research. Vol. 20, issue 11, 7878-7899.

3. McKay G. 1996. Use of Adsorbents for the Removal of Pollutants from Wastewaters. CRC Press, Inc. Hong Kong, 40-43.

4. Wolkersdorfer C. 2013. From Ground Water to Mine Water. Workshop on Mine Water Management and Remediation. Lappeenranta University of Technology, 2013. Conference. Finland. Mikkeli, 8-11.01.2013.

5. Sharma Y. 2013. A Guide to the Economic Removal of Metals from Aqueous Solutions. Wiley (Scrivener), 31-43.

6. Klaassen C. 2001. Casarett & Doull's, Toxicology, 6th edition. The Basic Science of Poisons. McGraw-Hill, 811-876.

7. European Commission. 2013. Urban Waste Water Directive Overview, 2013. WWW-document.
http://ec.europa.eu/environment/water/water-urbanwaste/.
Updated: 2013. Referred: 17.04.2013.

8. European Commission, 2001. Pollutants in urban wastewater and sewage sludge. PDF-document.
ec.europa.eu/environment/waste/sludge/pdf/sludge_pollutants.pdf.
Updated: 2001. Referred: 22.04.2013.

9. Fomkin A. 2009. Nanoporous Material and Their Adsorption Properties. Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Vol. 45, issue 2, 133–149.

10. Dabrowski A. 2001. Adsorption – from theory to practice, Advances in Colloid and Interface Science. Faculty of Chemistry, M.Curie-Sklodowska University, Lublin, Poland. Vol. 93, issue 1-3, 135-224.

11. Repo E. 2011. EDTA- and DTPA- Functionalized Silica Gel and Chitosan Adsorbents for the Removal of Heavy Metals From Aqueous Solutions. Lappeenranta University of Technology. Thesis.

12. Schlapbach L. 2009. Mechanisms of hydrogen storage. WWW-document. http://www.nature.com/nature/journal/v460/n7257/fig_tab/460809a_F2.html. Updated: 2009. Referred: 15.04.2013.

13. Willis T. 2009. Sorbents – Properties, Materials and Applications. Nova Science Publishers, Inc. New York, 52-104.

14. Chemical Systems 2013. Activated Carbon. WWW-document. http://www.chemsystem.ru/aktivirovannyy_ugol/. Updated: 2013. Referred: 02.03.2013.

15. Treatment Solutions, Lentech 2012. Activated Carbon. WWW-document. http://www.lenntech.com/library/adsorption/adsorption.htm. Updated: 2012. Referred: 02.03.2013.

16. Liu Grace. CO-sunny technology CO, Limited 2008. Activated Carbon. WWW-document. http://www.chem-hort.com/main/en_product_info.asp?id=641. Updated: 2008. Referred: 11.03.2013.

17. AquaVenture. Innovative Production Group. Zeolite 2012. WWW-document. http://aquaventure.ru/page_154_zeolite.html. Updated: 2012. Referred: 04.03.2013.

18. Sorbead India. Activated Alumina 2013. WWW-document. http://www.sorbeadindia.net/activated-alumina-345679.html.

Updated: 2013. Referred: 4.03.2013.

19. AquaVenture, Innovative Production Group. Activated Carbon 2012. WWW-document.
http://aquaventure.ru/page_153_oksid_aljuminija.html.
Updated: 2012. Referred: 04.03.2013.

20. China Silica Gel Co. WWW-document.
http://www.china-silicagel.com/product/fine-pore.html.
Updated: not available. Referred: 11.03.2013.

21. Environmental Protection, Chitosan 2010. WWW-document.
http://www.eco-oos.ru/biblio/sborniki-nauchnyh-trudov/ekologicheski-ustoichivoe-razvitie-racionalnoe-ispolzovanie-prirodnyh-resursov/62/.
Updated: 2010. Referred: 05.03.2013.

22. Made-in-China.com ™. Chitosan. WWW-document.
http://cnreachem.en.made-in-china.com/productimage/dMcxIiwhMSUB-2f0j00WMetYLBsCjrl/China-Chitosan-Nitrate.html.
Updated: not available. Referred: 11.03.2013.

23. SciVerse, ScienceDirect (Biotechnology Advances, Biosorbents) 2013. WWW-document.
http://www.sciencedirect.com/science/article/pii/S0734975008001109.
Updated: 2013. Referred: 05.03.2013.

APPENDIX 1(1).

Data from experiments

TABLE 4. Toxic Me (from solution 200 ppm) removal dependency on concentration of adsorbent with different concentrations (X1 and X2; g/L), time of sampling equals 1440 minutes

t=1440min	X1		X2	
C, g/L	Cu, ppm	Zn, ppm	Cu, ppm	Zn, ppm
0	200	200	200	200
2	200	199	199	199,9
5	187	198	187	199,9
10	170	196	180,2	194
15	152	192	150	179
20	137	190	120	140,9
30	121	120	75	80
40	99	78	30	30
50	12	49	1	0,5
60	12	48	1	0,5

TABLE 5. Toxic Me removal dependency (%) on concentration of adsorbent with different concentrations (X1 and X2; g/L), time of sampling equals 1440 minutes

t=1440min	Average	
C, g/L	X1 Cu & Zn, %	X2, Cu & Zn, %
0	0	0
2	0,25	0,275
5	3,75	3,275
10	8,5	6,45
15	14	17,75
20	18,25	34,775
30	39,75	61,25
40	55,75	85
50	84,75	99,625
60	85	99,625

TABLE 6. Adsorbent X1 with concentration 50 g/L, removal capacity depending on time periods, pH value at certain time

X1	t, min	Cu, ppm	Zn, ppm	pH
C=50g/L	0	200	200	1
	30	191,4	137,1	2,4
	60	146,6	103,8	2,4
	120	139,87	32,9	2,4
	180	32,9	55,3	3,3
	240	29,91	71,5	4,7
	300	30,6	70,1	4,7

360	31,8	72,3	4,9
420	22,5	69,9	5,4
480	13,9	69,1	5,4
720	13,8	67,2	5,9
1440	12,2	65,6	6,3

TABLE 7. Adsorbent X1 with concentration 50 g/L, removal capacity (%) depending on time periods, pH value at certain time

X1	t, min	Cu, %	Zn, %	pH
C=50g/L	0	0	0	1
	30	4,3	31,45	2,4
	60	26,7	48,1	2,4
	120	30,065	83,55	2,4
	180	83,55	72,35	3,3
	240	85,045	64,25	4,7
	300	84,7	64,95	4,7
	360	84,1	63,85	4,9
	420	88,75	65,05	5,4
	480	93,05	65,45	5,4
	720	93,1	66,4	5,9
	1440	93,9	67,2	6,3

TABLE 8. Adsorbent X2 with concentration 50 g/L, removal capacity depending on time periods, pH value at certain time

X2	t, min	Cu, ppm	Zn, ppm	pH
C=50g/L	0	200	200	1
	30	170,2	189,5	1,4
	60	117,4	62,3	1,4
	120	69,9	24,1	1,4
	180	100,2	48,1	1,4
	240	115,2	86,76	1,4
	300	119,1	42,2	1,3
	360	118,7	35,2	1,3
	420	119,3	35,5	1,4
	480	104,1	34,6	1,5
	720	70,7	39,5	1,5
	1440	1,4	0,51	1,5

TABLE 9. Adsorbent X2 with concentration 50 g/L, removal capacity (%) depending on time periods, pH value at certain time

X2	t, min	Cu, %	Zn, %	pH

C=50g/L	0	0	0	1
	30	14,9	5,25	1,4
	60	41,3	68,85	1,4
	120	65,05	87,95	1,4
	180	49,9	75,95	1,4
	240	42,4	56,62	1,4
	300	40,45	78,9	1,3
	360	40,65	82,4	1,3
	420	40,35	82,25	1,4
	480	47,95	82,7	1,5
	720	64,65	80,25	1,5
	1440	99,3	99,745	1,5

TABLE 10. Adsorbent X1 with concentration 50 g/L, removal capacity of Cu depending on time

X1/Cu	t, min	Cu ppm	C_{Cu}, mmol/l
C=50g/L	0	200	3,125000
	30	180	2,812500
	60	146,6	2,290625
	120	120	1,875000
	180	98	1,531250
	240	50	0,78125
	300	30,6	0,478125
	360	31,8	0,496875
	420	22,5	0,351563
	480	13,9	0,217188
	720	13,8	0,215625
	1440	12,2	0,190625

TABLE 11. Modelling adsorption kinetics of X1 for Cu by non-linear kinetic modelling of pseudo-first-order and pseudo-second-order

X1/Cu		Pseudo-first-order		Pseudo-second-order	
		qe	0,042062	qe	0,072236
Experimental kinetic data		k	1	k	0,079107
t	qt (mmol/g)	q (mmol/g)	ERRSQ	q (mmol/g)	ERRSQ
0	0	0	0	0	0
32	0,006250	0,042062	0,001283	0,011167121	2,42E-05
61	0,016687	0,042062	0,000644	0,018671479	3,94E-06
121	0,025000	0,042062	0,000291	0,029529326	2,05E-05
185	0,031875	0,042062	0,000104	0,037121746	2,75E-05
252	0,046875	0,042062	2,32E-05	0,042631569	1,8E-05

304	0,0529375	0,042062	0,000118	0,04584547	5,03E-05
362	0,0525625	0,042062	0,00011	0,048695898	1,5E-05
421	0,0554687	0,042062	0,00018	0,051026257	1,97E-05
482	0,0581562	0,042062	0,000259	0,052995545	2,66E-05
721	0,0581875	0,042062	0,00026	0,058127878	3,55E-09
1444	0,0586875	0,042062	0,000276	0,064428345	3,3E-05
		Sum	0,003548	Sum	0,000239

TABLE 12. Adsorbent X1 with concentration 50 g/L, removal capacity of Zn depending on time

X1/Zn	t, min	Zn ppm	C_{Cu}
C=50g/L	0	200	3,125000
	30	137,1	2,142188
	60	103,8	1,621875
	120	32,9	0,514063
	180	55,3	0,864063
	240	71,5	1,117188
	300	70,1	1,095313
	360	72,3	1,129688
	420	69,9	1,092188
	480	69,1	1,079688
	720	67,2	1,050000
	1440	65,6	1,025000

TABLE 13. Modelling adsorption kinetics of X1 for Zn by non-linear kinetic modelling of pseudo-first-order and pseudo-second-order

X1/Zn		Pseudo-first-order		Pseudo-second-order	
		qe	1	qe	1
Experimental kinetic data		k	1	k	1
t	qt (mmol/g)	q (mmol/g)	ERRSQ	q (mmol/g)	ERRSQ
0	0	0	9,24556E-07	0	9,25E-07
32	0,018694712	0,042062	0,000546054	0,011167	5,67E-05
61	0,029100962	0,042062	0,000168001	0,018671	0,000109
121	0,051257212	0,042062	8,45427E-05	0,029529	0,000472
185	0,044257212	0,042062	4,81676E-06	0,037122	5,09E-05
252	0,039194712	0,042062	8,22421E-06	0,042632	1,18E-05
304	0,039632212	0,042062	5,9063E-06	0,045845	3,86E-05
362	0,038944712	0,042062	9,7206E-06	0,048696	9,51E-05
421	0,039694712	0,042062	5,60642E-06	0,051026	0,000128
482	0,039944712	0,042062	4,48503E-06	0,052996	0,00017
721	0,040538462	0,042062	2,32269E-06	0,058128	0,000309
1444	0,041038462	0,042062	1,04865E-06	0,064428	0,000547

Sum	0,000841653	Sum	0,00199

TABLE 14. Adsorbent X2 with concentration 50 g/L, removal capacity of Cu depending on time

X2/Cu	t, min	Cu ppm	C_{Cu}
C=50g/L	0	200	3,125
	30	170,2	2,659375
	60	117,4	1,834375
	120	69,9	1,092187
	180	100,2	1,565625
	240	115,2	1,800000
	300	119,1	1,860937
	360	118,7	1,854687
	420	119,3	1,864062
	480	104,1	1,626562
	720	70,7	1,104687
	1440	1,4	0,021875

TABLE 15. Modelling adsorption kinetics of X2 for Cu by non-linear kinetic modelling of pseudo-first-order and pseudo-second-order

X2/Cu		Pseudo-first-order		Pseudo-second-order	
		qe	0,032227	qe	0,039612
Experimental kinetic data		k	1	k	0,607074
t	qt (mmol/g)	q (mmol/g)	ERRSQ	q (mmol/g)	ERRSQ
0	0	0	0	0	0
32	0,009312	0,032227	0,000525	0,017226	6,26E-05
61	0,025812	0,032227	4,11E-05	0,023555	5,1E-06
121	0,040656	0,032227	7,1E-05	0,02948	0,000125
185	0,031187	0,032227	1,08E-06	0,032342	1,33E-06
252	0,026500	0,032227	3,28E-05	0,034001	5,63E-05
304	0,025281	0,032227	4,82E-05	0,034845	9,15E-05
362	0,025406	0,032227	4,65E-05	0,03553	0,000102
421	0,025218	0,032227	4,91E-05	0,036051	0,000117
482	0,029968	0,032227	5,1E-06	0,036466	4,22E-05
721	0,040406	0,032227	6,69E-05	0,037452	8,73E-06
1444	0,0620625	0,032227	0,00089	0,038503	0,000555
		Sum	0,001777	Sum	0,001168

TABLE 16. Adsorbent X2 with concentration 50 g/L, removal capacity of Zn depending on time

X2/Zn	t min	Zn ppm	C mmol/l

C=50g/L	0	200	3,0769231
	30	189,5	2,9153846
	60	62,3	0,9584615
	120	24,1	0,3707692
	180	48,1	0,7400000
	240	86,76	1,3347692
	300	42,2	0,6492308
	360	35,2	0,5415385
	420	35,5	0,5461538
	480	34,6	0,5323077
	720	39,5	0,6076923
	1440	0,5	0,0076923

TABLE 17. Modelling adsorption kinetics of X2 for Zn by non-linear kinetic modelling of pseudo-first-order and pseudo-second-order

X2/Zn		Pseudo-first-order		Pseudo-second-order	
		qe	0,044815	qe	0,058004
Experimental kinetic data		k	1	k	0,313307
t	qt (mmol/g)	q (mmol/g)	ERRSQ	q (mmol/g)	ERRSQ
0	0	0	0	0	0
32	0,00323077	0,044814825	0,001729	0,021328	0,000328
61	0,04236923	0,044814825	5,98E-06	0,030495	0,000141
121	0,05412308	0,044814825	8,66E-05	0,039872	0,000203
185	0,04673846	0,044814825	3,7E-06	0,044707	4,13E-06
252	0,03484308	0,044814825	9,94E-05	0,047608	0,000163
304	0,04855385	0,044814825	1,4E-05	0,049114	3,14E-07
362	0,05070769	0,044814825	3,47E-05	0,050351	1,28E-07
421	0,05061538	0,044814825	3,36E-05	0,051299	4,67E-07
482	0,05089231	0,044814825	3,69E-05	0,052061	1,37E-06
721	0,04938462	0,044814825	2,09E-05	0,053891	2,03E-05
1444	0,06138462	0,044814825	0,000275	0,055875	3,04E-05
		Sum	0,00234	Sum	0,000892

TABLE 18. Modelling adsorption isotherms of X1 for Cu by Langmuir and Freundlich isotherm models

X1, Cu			
C, g/L	Cu ppm	C mmol/g	C_{ads} mmol/g
2	200	3,125000	0
5	187	2,921875	0,203125
10	170	2,656250	0,468750
15	152	2,375000	0,750000

20	137	2,140625	0,984375
30	121	1,546875	1,578125
40	99	0,828125	2,296875
50	12	0,187500	2,937500
Cu		qm	0,05765757
Langmuir		K	10,5114123
experiment	experiment	model	
Ceq (mmol/L)	qeq (mmol/L)	qeq (mmol/L)	ERRSQ
0	0	0	0
0,2031	0,040625	0,039265224	1,849E-06
0,4063	0,046875	0,046718487	2,4496E-08
0,7500	0,050000	0,0511672	1,3624E-06
0,9844	0,049218	0,052576458	1,1274E-05
1,5781	0,052604	0,054379346	3,1513E-06
2,2969	0,057421	0,055364443	4,233E-06
2,9375	0,058750	0,055848833	8,4168E-06
		Sum	3,0311E-05
Cu		n	5,39612041
Freundlich		K	0,04952103
experiment	experiment	model	
Ceq (mmol/L)	qeq (mmol/L)	qeq (mmol/L)	ERRSQ
0	0	0	0
0,2031	0,040625	0,036854931	1,4213E-05
0,4063	0,046875	0,041908468	2,4666E-05
0,7500	0,050000	0,046950066	9,3021E-06
0,9844	0,049218	0,049376945	2,5026E-08
1,5781	0,052604	0,053889927	1,6532E-06
2,2969	0,057421	0,057771799	1,2245E-07
2,9375	0,058750	0,060466456	2,9462E-06
		Sum	5,2929E-05

TABLE 19. Modelling adsorption isotherms of X1 for Zn by Langmuir and Freundlich isotherm models

X1, Zn			
C, g/L	Zn ppm	C mmol/g	C_{ads} mmol/g
2	199	3,061538462	0,015384615
5	198	3,046153846	0,030769231
10	196	3,015384615	0,061538462
15	192	2,953846154	0,123076923
20	190	2,923076923	0,153846154
30	120	1,846153846	1,230769231
40	78	1,230769231	1,846153846
50	49	0,769230769	2,307692308

Zn		qm	0,066314578
Langmuir		K	1,130942311
experiment	experiment	model	
Ceq (mmol/L)	qeq (mmol/L)	qeq (mmol/L)	ERRSQ
0,015384615	0,007692308	0,001134083	4,30103E-05
0,030769231	0,006153846	0,002230029	1,53963E-05
0,061538462	0,006153846	0,004314954	3,38153E-06
0,123076923	0,008205128	0,008102683	1,04951E-08
0,153846154	0,007692308	0,009828139	4,56178E-06
1,230769231	0,041025641	0,038590269	5,93104E-06
1,846153846	0,046153846	0,044838909	1,72906E-06
2,307692308	0,046153846	0,047944211	3,20541E-06
		Sum	7,7226E-05
Zn		n	0,863496227
Freundlich		K	0,967297073
experiment	experiment	model	
Ceq (mmol/L)	qeq (mmol/L)	qeq (mmol/L)	ERRSQ
0,015384615	0,007692308	0,007692303	2,47557E-17
0,030769231	0,006153846	0,025978253	0,000393007
0,061538462	0,006153846	0,029539036	0,000546867
0,123076923	0,008205128	0,033587888	0,000644284
0,153846154	0,007692308	0,035005952	0,000746035
1,230769231	0,041025641	0,051463702	0,000108953
1,846153846	0,046153846	0,055479682	8,69712E-05
2,307692308	0,046153846	0,057822007	0,000136146
		Sum	0,002662264

TABLE 20. Modelling adsorption isotherms of X2 for Cu by Langmuir and Freundlich isotherm models

X2, Cu			
C/g/L	Cu ppm	C mmol/g	C_{ads} mmol/g
2	199	3,109375	0,015625
5	187	2,921875	0,203125
10	180,2	2,815625	0,309375
15	150	2,34375	0,78125
20	120	1,875	1,25
30	75	1,171875	1,953125
40	30	0,46875	2,65625
50	1	0,015625	3,109375
Cu		qm	0,070316418
Langmuir		K	4,328173092
experiment	experiment	model	
Ceq (mmol/L)	qeq (mmol/L)	qeq (mmol/L)	ERRSQ

0,015625	0,007812	0,004454116	1,12787E-05
0,203125	0,040625	0,032897352	5,97165E-05
0,309375	0,030937	0,040254186	8,68006E-05
0,78125	0,052083	0,054267517	4,77066E-06
1,25	0,062500	0,059346988	9,94149E-06
1,953125	0,065104	0,062878253	4,95469E-06
2,65625	0,066406	0,064689623	2,94681E-06
3,109375	0,062187	0,065452893	1,06628E-05
		Sum	0,000191072
Cu		n	3,656159706
Freundlich		K	0,051568183
experiment	experiment	model	
Ceq (mmol/L)	qeq (mmol/L)	qeq (mmol/L)	ERRSQ
0,015625	0,007812	0,016533762	7,60604E-05
0,203125	0,040625	0,033346286	5,29797E-05
0,309375	0,030937	0,037413119	4,19336E-05
0,78125	0,052083	0,048201296	1,50702E-05
1,25	0,062500	0,054813532	5,90818E-05
1,953125	0,065104	0,061929803	1,00766E-05
2,65625	0,066406	0,06736341	9,16155E-07
3,109375	0,062187	0,070328824	6,62812E-05
		Sum	0,0003224

TABLE 21. Modelling adsorption isotherms of X2 for Zn by Langmuir and Freundlich isotherm models

X2, Zn			
C/g/L	Zn ppm	C mmol/g	C_{ads} mmol/g
2	199,9	3,075385	0,001538
5	199,9	3,075385	0,001538
10	194	2,984615	0,092308
15	179	2,753846	0,323077
20	140,9	2,167692	0,909231
30	80	1,230769	1,846154
40	30	0,461538	2,615385
50	0,5	0,007692	3,069231
Zn		qm	0,082206
Langmuir		K	1,289027
experiment	experiment	model	
Ceq (mmol/L)	qeq (mmol/L)	qeq (mmol/L)	ERRSQ
0,001538	0,000769	0,000163	3,68E-07
0,001538	0,000308	0,000163	2,1E-08
0,092308	0,009231	0,008741	2,4E-07

0,323077	0,021538	0,024170	6,92E-06
0,909231	0,045462	0,044358	1,22E-06
1,846154	0,061538	0,057883	1,34E-05
2,615385	0,065385	0,063400	3,94E-06
3,069231	0,061385	0,065620	1,79E-05
		Sum	4,4E-05
Zn		n	2,205087
Freundlich		K	0,041468
experiment	experiment	model	
Ceq (mmol/L)	qeq (mmol/L)	qeq (mmol/L)	ERRSQ
0,001538	0,000769	0,002198	2,04E-06
0,001538	0,000308	0,002198	3,57E-06
0,092308	0,009231	0,014075	2,35E-05
0,323077	0,021538	0,024842	1,09E-05
0,909231	0,045462	0,039717	3,3E-05
1,846154	0,061538	0,054760	4,59E-05
2,615385	0,065385	0,064131	1,57E-06
3,069231	0,061385	0,068957	5,73E-05
		Sum	0,000178

APPENDIX 2(1).

Figures

FIGURE 24. Scales Sartorius model SPA225D

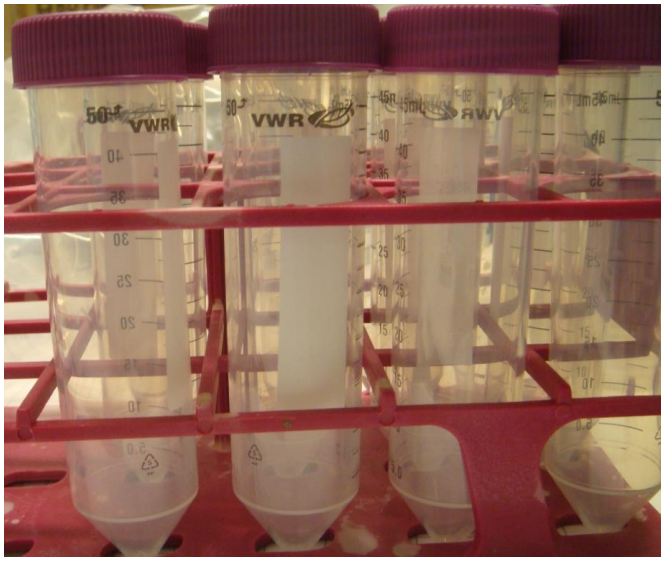

FIGURE 25. Cylindrical plastic tubes 50 ml with caps

APPENDIX 2(2).

Figures

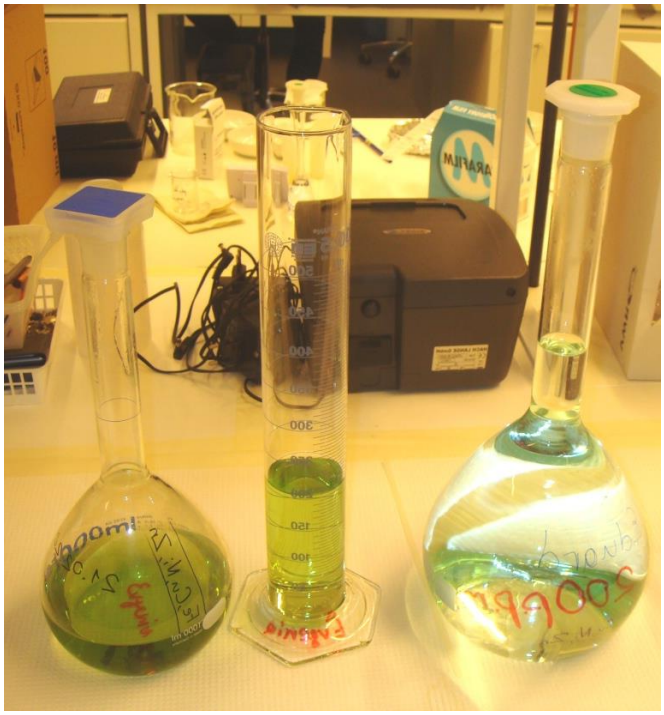

FIGURE 26. Solution of Cu((II) $Cu(NO_3)_2*3H_2O$, m=3,781 g) and Zn((II) $ZnSO_4*7H_2O$, m=4,415) mixed in water with the addition of HNO_3, right 1000 ml flask and 500 ml cylinder have 1000 ppm of those studied Me, left 2000 ml flask was made in accordance to the concentration of studied 200 ppm

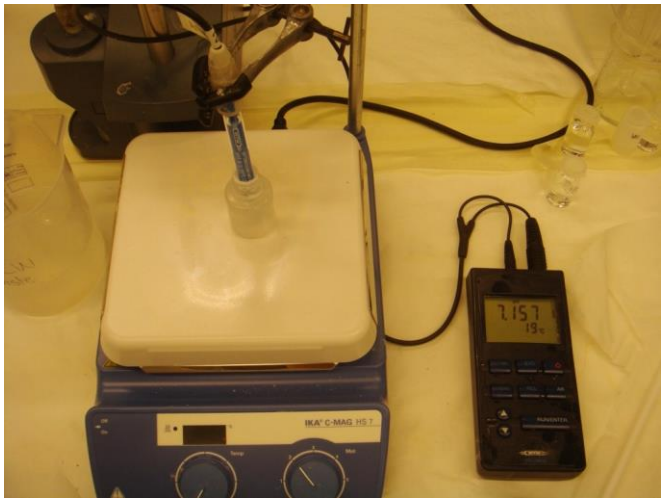

FIGURE 27. From the left side is heating plate model IKA C-MAG HS7 with a regulated magnet field for mixing solutions, on the right side pH meter model WTW pH 340i

APPENDIX 2(3).

Figures

FIGURE 28. Assembled 10 ml plastic syringe with polypropylene membrane filter (25 mm syringe filter w/0.45 um polypropylene membrane (VWR International, USA))

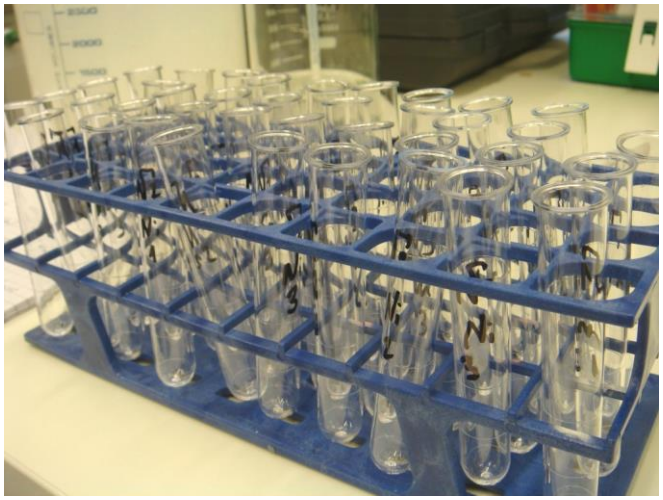

FIGURE 29. 10 ml plastic cylindrical tubes

FIGURE 30. iCAP 6000 Series (inductivity coupled plasma optical atomic emission spectrometry (ICP-OES)) was used to determine the metal concentrations in the solution

APPENDIX 2(4).

Figures

FIGURE 31. AutoSampler ASX-260, synchronized with iCAP 6000 Series to inject studied samples into ICP reactor

FIGURE 32. Zetasizer Nano Series model ZEN 3600 (Malvern, the UK), was used to determine isoelectric points of the solutions

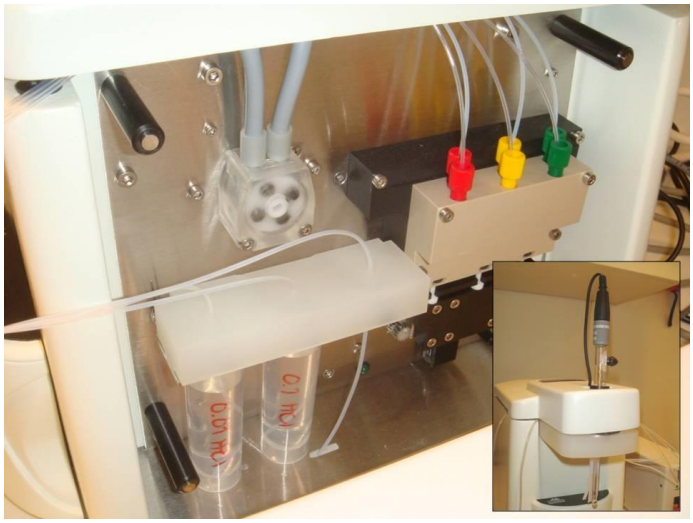

FIGURE 33. Zetasizer Nano Series model ZEN 3600 (Malvern, the UK), another part which aimed at titration, on the picture shown slot for titrants (for one sets of experiments were used HCL 0,01 M, 0,1 M the last slot was empty)

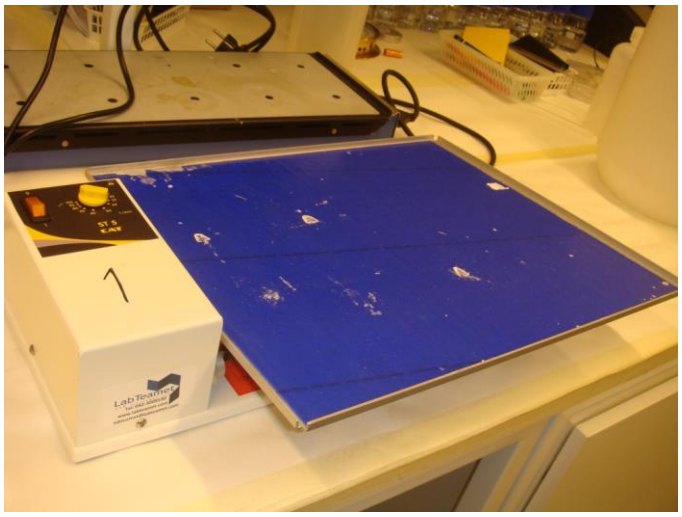

FIGURE 34. Rotary shaker, CAT ST5